**TOXINS** 

# WORKING DRAFT

5 BAY DELTA CONSERVATION PLAN

**January 2012** 





3

# **Contents**

5			Page
6	Appendix D Toxi	ins	D-1
7	D.1 Exec	cutive Summary	D-1
8	D.2 Orga	anization of Appendix	D-6
9	D.3 Over	rview of Toxins as Stressors	D-7
10	D.3.1	Selection of Toxin Stressors for Analysis	D-7
11	D.4 Meth	hods	D-11
12	D.4.1	Problem Formulation	D-11
13	D.4.2	Conceptual Model	D-12
14	D.5 Resu	ults—Effects of Preliminary Proposal Conservation Measures on Toxins	D-14
15	D.5.1	Mercury	D-14
16	D.5.2	Selenium	
17	D.5.3	Copper	D-39
18	D.5.4	Ammonia/um	
19	D.5.5	Pyrethroids	
20	D.5.6	Organochlorine Pesticides	
21	D.5.7	Organophosphate Pesticides	
22	D.5.8	Other Urban Contaminants	
23		cts of Changes in Toxins on Covered Fish Species	
24	D.6.1	Summary of Conclusions	
25	D.6.2	Conclusion of Effects of Toxins on Covered Fish Species	
26	D.6.3	Uncertainties and Information Needs	
27	(3)	rences	
28	D.7.1	Printed References	D-61
29	D.7.2	Personal Communications	D-65
30			
31	Attachment D.A	Bioaccumulation Model Development for Mercury Concentrations in Fish	1
32	Attachment D.B	Selenium Modeling Methods	

# **Tables**

2		Page
3	Table D-1. Potential for Effects of Toxins on Covered Fish Species from the Preliminary Proposal	D-4
4	Table D-2. Land Use and Typically Associated Contaminant Issues	D-7
5	Table D-3. Clean Water Act 2010 Section 303(d) Listed Pollutants and Sources in the Plan Area	D-9
6	Table D-4. Summary of Completed and Ongoing Total Maximum Daily Loads in the Delta	D-10
7	Table D-5. Mercury and Methylmercury TMDLs in the Delta and San Francisco Bay	D-15
8	Table D-6. Historical Methylmercury Concentrations in the Five Delta Source Waters for the Perio	d
9	2000–2008	D-18
10	Table D-7. Modeled Mercury Concentrations in Water: Early Long-Term	D-19
11	Table D-8. Modeled Methylmercury Concentrations in Water: Early Long-Term	
12	Table D-9. Modeled Mercury Concentrations in Largemouth Bass Fillets: Early Long-Term	D-21
13	Table D-10. Modeled Mercury Concentrations in Water: Late Long-Term	D-22
14	Table D-11. Modeled Methylmercury Concentrations in Water: Late Long-Term	D-23
15	Table D-12. Modeled Mercury Concentrations in Largemouth Bass Fillets: Late Long-Term	
16	Table D-13. Applicable Federal Criteria, State Standards/Objectives, and Other Relevant Effect	
17	Thresholds for Selenium	D-27
18	Table D-14. Historical Selenium Concentrations in the Five Delta Source Waters for the Period	
19	1996–2010	D-31
20	Table D-15. Modeled Selenium Concentrations in Water for Early Long-Term	D-32
21	Table D-16. Modeled Selenium Concentrations in Water for Late Long-Term	D-33
22	Table D-17. Modeled Selenium Concentrations in Fish Fillets for Early Long-Term	
23	Table D-18. Modeled Selenium Concentrations in Fish Fillets for Late Long-Term	D-35
24	Table D-19. Modeled Selenium Concentrations in Whole-Body Fish for Early Long-Term	D-36
25	Table D-20. Modeled Selenium Concentrations in Whole-Body Fish for Late Long-Term	D-37
26	Table D-21. Difference in Annual Average Proportion of San Joaquin River Contribution to Water	
27	Flow at South Delta and Suisun Bay	D-38
28	Table D-22. Ambient Water Quality Criteria for Ammonia	D-42
29	Table D-23. Sacramento and Stockton Wastewater Treatment Facility Effluent—	
30	National Pollution Discharge Elimination System Permit Limits	D-43
31	Table D-24. Sacramento River Flow Required to Dilute Sacramento Wastewater Treatment Plant	
32	Effluent	D-44
33	Table D-25. Percentage of Months in CALSIM (82 Years) That Flows Are below Threshold (5,794	
34	cfs) for Adequate Dilution of Sacramento WWTP Effluent to <1.2 mg/L Ammonia	D-45
35	Table D-26. Percent Increase in the Number of Months That Flows Are below Threshold (5,794 cfs	<b>s</b> )
36	for Adequate Dilution of Sacramento WWTP Effluent to <1.2 mg/L Ammonia	D-45
37	Table D-27. Estimation of Resultant Pyrethroid Concentrations in Water under Preliminary	
38	Proposal Low-Flow Conditions in the Sacramento River	D-47
39	Table D-28. Summary of Toxicity Testing for Invasive Species Herbicides	D-51
40		

# **Figures**

- 2 Appear at the end of the appendix.
- 3 Figure D-1 Generic Conceptual Model to Evaluate Preliminary Proposal Toxins Effects
- 4 Figure D-2 Methylmercury Cycling in Aqueous System

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# **Acronyms and Abbreviations**

 $\mu g/g$  micrograms per gram  $\mu g/L$  micrograms per liter

AWQC ambient water quality criteria

Bay-Delta San Francisco Bay-Sacramento-San Joaquin River Delta

BDCP Bay-Delta Conservation Plan

cfs cubic feet per second
CM Conservation Measure
CRT Criterion Total Recoverable

 $\begin{array}{cc} \text{Cu} & \text{copper} \\ \text{Cu}^{2+} & \text{cupric ion} \end{array}$ 

DBW California Department of Boating and Waterways

DDD Dichlorodiphenyldichloroethane
DDE Dichlorodiphenyldichloroethene
DDT Dichlorodiphenyltrichloroethane
Delta Sacramento-San Joaquin River Delta

DOC dissolved organic carbon

DRERIP Delta Regional Ecosystem Restoration Implementation Plan

EDC Endocrine-disrupting compounds

EEQ estradiol equivalent

EIS/EIR environmental impact statement/environmental impact report

EPA U.S. Environmental Protection Agency

FRV Final Residual Value kg/yr kilograms per year LLT late-long-term

ng/L nanograms per liter (equivalent to 1 part per trillion, or ppt)

NH3+ ammonia (also referred to as un-ionized ammonia)

NH4+ ammonium ion

NMFS National Marine Fisheries Service

NPDES National Pollutant Discharge Elimination System

NTR National Toxics Rule

OEHHA Office of Environmental Health Hazard Assessment

PCBs Polychlorinated biphenyls
POD pelagic organism decline
ROAs restoration opportunity areas

 $\begin{array}{lll} \text{Se} & & \text{selenium} \\ \text{Se}^{2-} & & \text{selenides} \\ \text{Se}^{4+} & & \text{selenites} \\ \text{Se}^{6+} & & \text{selenates} \end{array}$ 

TMDL total maximum daily load USFWS U.S. Fish and Wildlife Service

USGS U.S. Geological Survey

WWTP wastewater treatment plant

Appendix D **Toxins** 

# **D.1** Executive Summary

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Toxins have been identified as adverse stressors in the Delta ecosystem and have been associated with pelagic organism decline (POD) (Baxter et al. 2010; Glibert 2010; Glibert et al. 2011). Some of these toxins are contaminants that have been introduced to the ecosystem, and others are naturally occurring constituents in the Delta that have been mobilized and/or concentrated by anthropogenic activities. Although contaminants in water can be directly lethal to biota at very high concentrations, toxins usually occur at concentrations much below lethal levels, enter the food chain at lower trophic levels, and can become more concentrated higher up in the food chain. Sublethal levels in fish result in various effects, including impaired growth and reproduction, and increase in the organism's susceptibility to disease (Werner et al. 2008).

The preliminary proposal (PP) will not introduce new toxins or increase the concentrations of toxins in the Plan Area directly, , with the exception of herbicides, which would be applied in limited and safe concentrations to control invasive aquatics weeds. However, the PP includes restoration and changes in water operations that have the potential to change how toxins already present in the Plan Area are mobilized and transported in the Plan Area. To determine whether PP actions would influence the exposure to and effects of toxins on covered fish species, potential mechanisms for PP actions to result in increased concentrations and bioavailability of toxins first were identified and evaluated. This was achieved by developing conceptual models that included all factors that influence the environmental fate and transport, mobility in an aquatic system, and bioavailability to covered fish species for each toxin. Quantitative analyses are applied where they were useful in describing factors within the conceptual models, and if data inputs and available analytical and modeling tools were deemed sufficient to provide reliable results. As discussed in this appendix, given the complex nature of toxin biogeochemistry, area hydrology, and behavior and physiology of covered fish species that together determine the effects of toxins, quantitative analyses alone were not sufficient to fully examine potential effects. The environmental toxins evaluated in this appendix were selected based on historical and current land use along with published literature regarding water quality in the Delta and the types of toxins that have effects on fish.

- 31 

  Selenium
- 32 Copper
- 33 a Ammonia/um
- 34 Pesticides
- 35 Pyrethroids
- 36 Organochlorines
- 37 Organophosphates

Based on results of the evaluation presented in this appendix, PP water operations are not expected to affect toxins significantly in the Sacramento–San Joaquin River Delta (Delta) through either increased mobilization or transport. Two primary pathways of effects on toxins were examined in connection with water operations, an increase in the proportional amount of flow from the San Joaquin River and a reduction in flow in the Sacramento River.

The first pathway is the potential for increased loading of selenium from increased contributions of water from the San Joaquin watershed as Sacramento River inputs were diverted by north Delta intakes. Based on the evaluation of current and expected future reductions in selenium from the San Joaquin watershed, and source-water fingerprinting that indicates no increase of San Joaquin water contribution at Suisun Marsh and a only a slight increase in the south Delta, minimal effects on selenium or associated effects on covered fish species are expected.

The second issue connected to PP water operations is the potential for decreased dilution capacity of the Sacramento River, especially for Sacramento Regional Wastewater Treatment Plant (WWTP) effluent, and more specifically for ammonia and pyrethroids. Modeling results presented in Appendix C indicate that reduced dilution capacity in the Sacramento River at the Sacramento WWTP will result from changes in upstream reservoir operations associated with the PP, not from diversion of water to the Yolo Bypass or from north Delta intakes located downstream of the WWTP. Quantitative analysis presented in this appendix indicates that the Sacramento River will have sufficient dilution capacity under the PP for both ammonia and pyrethroids to avoid adverse effects from these toxins on the covered fish.

Restoration actions will result in some level of mobilization and increased bioavailability of methylmercury, copper, and pesticides (including organophosphate, organochlorine and pyrethroid pesticides). Given current information, it is not possible to estimate the concentrations of these constituents that will become available to covered fish species, but review of the conceptual models for each of these toxins indicates that the effects should be limited both temporally and spatially. The most problematic of these potential effects is methylmercury. To address this issue, the Plan includes Conservation Measure (CM) 12 Methylmercury Management, which provides for site-specific assessment of restoration areas, integration of design measures to minimize methylmercury production, and site monitoring and reporting. The areas with the highest potential for methylmercury generation are the Yolo Bypass, and to a lesser extent, the Mokelumne-Cosumnes River. With the implementation of CM12, effects of methylmercury mobilization on covered fish at the tidal wetland restoration sites are expected to be minimized.

In general, the following conclusions can be drawn.

- Preliminary proposal water operations will have few to no effects on toxins in the Delta.
- Preliminary proposal restoration will increase bioavailability of certain toxins, especially methylmercury, but the overall effects on covered fish species are expected to be localized and of low magnitude.
  - Available data suggest that species exposure to toxins would be below sublethal and lethal levels.
- The long-term benefits of restoration will reduce exposure to existing toxins in the environment and eliminate sources.

A summary of conclusions from the toxins analysis is presented in Table D-1. The color coding in the table is based on consideration of the potential for an increase in the bioavailability of toxins due to

preliminary proposal actions, presence of covered fish species/life stages, and expected potential for effects on covered species/life stage. Based on this analysis, none of the scenarios was rated as *High* potential for effects.

- None—Areas with potential for increase in toxins due to the PP, but susceptible life stage of covered species is absent (also applies if there is fish occurrence, but no toxins).
- □ **Low**—Areas with potential for increase in toxins due to PP and susceptible life stage of covered species present, but evaluation shows little potential for effects.
- ☐ **Moderate**—Same as *Low*, but evaluation shows moderate potential for effects.

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High—Same as *Moderate*, but evaluation shows high potential for effects based on mobilization of toxins into the foodweb and effects on covered fish species.



Table D-1. Potential for Effects of Toxins on Covered Fish Species from the Preliminary Proposal

		BDCP Regions									
Species	Life Stage	Yolo Bypass	Cache Slough	North Delta	West Delta	Suisun Bay	Suisun Marsh	East Delta	South Delta		
Delta smelt	Eggs	M, C	M, C	C, S, P*	C, S, P		M, S*	M*	S, P*		
	Larva	M, C	M, C	C, S, P*	C, S, P	S	M, S*	M*	S, P*		
	Juvenile	M, C	M, C	C, S, P*	C, S, P	S	M, S*	M*	S, P*		
	Adult	M, C	M, C	C, S, P*	C, S, P	S	M, S*	M*	S, P*		
Longfin smelt	Eggs	M, C	M, C	C, S, P*	C, S, P		M, S				
	Larva	M, C	M, C	C, S, P*	C, S, P	S	M, S	M*	S, P		
	Juvenile	M, C	M, C	C, S, P*	C, S, P	S	M, S		S, P		
	Adult	M,C	M, C	C, S, P*	C, S, P	S	M, S		S, P		
Steelhead	Egg/Embryo										
	Fry										
	Juvenile	M, C	M, C	C, S, P	C, S, P	S	M, S	М	S, P		
	Adult	M, C	M, C	C, S, P	C, S, P	S	M, S	M	S, P		
Winter-run	Egg/Embryo										
Chinook salmon	Fry	M, C	M, C	C, S, P	C, S, P						
	Juvenile	M, C	M, C	C, S, P	C, S, P	S	M, S	М	S, P		
	Adult	M, C	M, C	C, S, P	C, S, P	S	M, S	M			
Spring-run	Egg/Embryo										
Chinook salmon	Fry	M, C	M, C	C, S, P	C, S, P			1.00			
	Juvenile	M, C	M, C	C, S, P	C, S, P	S	M, S	M	S, P		
	Adult	M, C	M, C	C, S, P	C, S, P	S	M, S	M			
Fall-/late fall-run	Egg/Embryo										
Chinook salmon	Fry	M, C	M, C	C, S, P	C, S, P	S	M, S	M	S, P		
	Juvenile	M,C	M, C	C, S, P	C, S, P	S	M, S	М	S, P		
	Adult	M, C	M, C	C, S, P	C, S, P	S	M, S	M	S, P		

		BDCP Regions									
Species	Life Stage	Yolo Bypass	Cache Slough	North Delta	West Delta	Suisun Bay	Suisun Marsh	East Delta	South Delta		
Sacramento	Egg/Embryo	M		C, S, P*			M, S	M	S, P		
splittail	Larvae	М		C, S, P*			M, S	М	S, P		
	Juvenile	M	M	C, S, P*	C, S, P	S	M, S	М	S, P		
	Adult	М	M	C, S, P*	C, S, P	S	M, S	М	S, P		
White sturgeon	Egg/Embryo										
	Larva	М	M	C, S, P*	C, S, P			М	S, P		
	Juvenile	M	M	C, S, P*	C, S, P	S	M, S	M	S, P		
	Adult	M	M	C, S, P*	C, S, P	S	M, S	M	S, P		
Green sturgeon	Egg/Embryo										
	Larva										
	Juvenile	M, C	M, C	C, S, P*	C, S, P*	S*	M, S*	M*	S, P*		
	Adult	M, C	M, C	C, S, P*	C, S, P*	S*	M, S*	M*	S, P*		
Pacific lamprey	Egg/Embryo										
	Ammocoete	M, C	M, C	C, S, P*	C, S, P*			М	S, P*		
	Macropthalmia	M,C	M, C	C, S, P*	C, S, P*	S*	S*	M*	S, P*		
	Adult	M, C	M, C	C, S, P*	C, S, P*	S*	M, S*	M*	S, P*		
River lamprey	Egg/Embryo										
	Ammocoete	M, C	M, C					М			
	Macropthalmia	M, C	M, C	C, S, P*	C, S, P*	S*	M, S*	M*	S, P*		
	Adult	M, C	M, C	C, S, P*	C, S, P*	S*	M, S*	M*	S, P*		

<sup>\*</sup> Scoring partially based on low abundance of species/life stage in the area.

M = mercury, P = pesticides, S = selenium, C = copper

Categories of effect of toxin as result of BDCP:

	1620 EV 1000 E	
None		
Low		
Medium		
High		

D-5

# **D.2** Organization of Appendix

This appendix presents a discussion of the toxins that are widely recognized as significant to determining the potential of the Delta ecosystem to support covered fish species, and how potential changes to toxins caused by the preliminary proposal could affect covered fish species. To do this, the appendix provides a general overview of toxic constituents currently present in the Delta aquatic ecosystem, identifies and assesses changes in toxins that could result from implementation of the preliminary proposal, and describes how those changes could result in changes in exposure of covered fish species to toxins. The analysis focuses only on changes in toxins that are directly attributable to the preliminary proposal actions that could affect covered fish species.

Water quality parameters, including salinity, turbidity, and temperature, are integrated with the hydrologic flow analyses and are discussed in Appendix C. Results of the flow analysis are included in this appendix where they support analysis of toxins. This appendix discusses only covered fish species. Ecological effects, including food chain and organisms other than covered fish species, are evaluated in Appendix F, *Ecological Effects*.

The approach in this toxins analysis is to develop a complete picture of all factors that contribute to the bioavailability and effects of these toxins on covered fish species. Qualitative conceptual models are presented that capture and describe all determining factors. The conceptual models draw from those developed by the Delta Regional Ecosystem Restoration Implementation Plan (DRERIP), along with other relevant information sources. Quantitative analyses are used where they are useful in describing factors within the conceptual models, and if data inputs and available analytical and modeling tools are deemed sufficient to provide reliable results. As discussed in this appendix, given the complex nature of toxin biogeochemistry, area hydrology, and behavior and physiology of covered fish species that together determine the effects of toxins, quantitative analyses alone were not sufficient to fully examine potential effects.

The analyses in this appendix are presented in two steps. The first step identifies effects on toxins that are directly attributable to preliminary proposal actions. The second step evaluates the potential for these changes in toxins to affect covered fish species, at what life stages, and where in the preliminary proposal study area. The general approach to the analysis for each toxic constituent is outlined below.

- Determine effects of preliminary proposal actions on potentially toxic constituents in the Delta ecosystem.
  - a. Describe the environmental chemistry of each parameter, the source of the element, how it is transported in the environment, and where it tends to accumulate.
  - Discuss preliminary proposal actions that could result in changes in toxic water constituents, at what locations and when (if there is a seasonal component).
- 2. Determine effects of changes in potentially toxic constituents on covered fish species.
  - a. Compare the spatial/temporal occurrence of each covered fish species/life stage with changes in toxins, identifying where changes in toxins coincide temporally and spatially with the presence of covered fish species.
  - b. Discuss how preliminary proposal-induced changes to toxins could affect covered fish species/life stages in the Delta.

## D.3 Overview of Toxins as Stressors

Stressors act on the environment by changing flow, water quality, temperature, or other attributes that determine the suitability of habitat for a species. Toxins have been identified as adverse stressors in the Delta ecosystem and have been associated with POD (Baxter et al. 2010; Glibert 2010; Glibert et al. 2011). Some of these toxins are contaminants that have been introduced to the ecosystem, and others are naturally occurring constituents in the Delta that have been mobilized and/or concentrated by anthropogenic activities. Although contaminants in water can be directly lethal to biota at very high concentrations, contaminants usually occur at concentrations much below lethal levels, enter the food chain at lower trophic levels, and can become more concentrated higher up in the food chain. Sublethal levels in fish result in various effects, including impaired growth and reproduction, and increase in the organism's susceptibility to disease (Werner et al. 2008).

## **D.3.1** Selection of Toxin Stressors for Analysis

Water quality characteristics and the presence of contaminants (toxins) in the environment are determined by both natural conditions and land use. The primary land uses affecting toxins in the Delta include historical mining operations in the mountains drained by Delta tributaries, agriculture in the Delta and tributaries, discharges related primarily to rural human habitation (wastewater), and discharges related to urban development (stormwater runoff, municipal wastewater, industrial wastewater). The types of contaminant issues typically associated with these land uses are presented in Table D-2 and discussed further in the following paragraphs.

Table D-2. Land Use and Typically Associated Contaminant Issues

Land Use	Typical Discharges/Operations	Typical Contamination Issues
Mining (historical)	Concentrated mining waste	Mercury and copper (specific to mining operations local to Delta)
Agriculture	Fertilizers Pesticides Drainage	Nutrients (ammonia) Copper Pesticides Selenium*
Rural human habitation	Wastewaterdischarge	Nutrients (ammonia)
Urban development	Municipal wastewater treatment plant discharge Stormwater runoff	Nutrients (ammonia), pesticides, endocrine disruptors Metals, pesticides, petroleum residues (PAHs)
* Colonium from a guioultu	Industrial waste discharges	Metals, PCBs (from historical discharges)

\* Selenium from agricultural drainage is specific to locations like the Delta that have high levels of naturally occurring selenium in soils, which are concentrated in agricultural drainage.

Historical mining of mercury and gold resulted in concentrating and mobilizing certain metals that occur naturally in the mountains of the upper tributaries. Metals are present in rocks, soils, and sediments to varying degrees, dependent on the source rocks. During the mining process, naturally occurring metals were mobilized, transported via streams, and deposited in sediments of the Delta marshes, wetlands, and streambeds.

Agriculture has been the primary land use in the Delta for more than a century (Wood et al. 2010). In the Plan Area, 503,779 acres (59%) are used for agriculture (see Chapter 2, *Existing Conditions*). The pesticides, herbicides, and fertilizers applied to agricultural lands throughout the Delta are present in the soils where they were applied but also have migrated off the farmed properties via air, groundwater, runoff, and rivers and are dispersed throughout all environmental media in the Delta ecosystem. The majority of pesticides used in the Delta fall into three families of pesticides—organochlorides (including dichlorodiphenyltrichloroethane [DDT]) were used historically and now are banned, and pyrethroids and organophosphates are currently in use.

Rural developments associated with agricultural land use have minimal discharge of toxins. The main types of discharges are relatively small volumes of wastewater, typically through local septic systems.

Cities and towns account for only 8% of the Plan Area (70,174 acres). The main urban centers are the cities of Sacramento and West Sacramento located on the Sacramento River, and the city of Stockton located on the San Joaquin River (Wood et al. 2010). Although urban development accounts for a small percentage of land use in the Delta, urban discharges have affected the aqueous environment. Release of toxins to water typically associated with urban development is related to stormwater and WWTP discharges.

Stormwater typically is characterized by varying levels of metals, pesticides, and hydrocarbons that can accumulate in river sediments over time. Historically, polychlorinated biphenyls (PCBs) often were associated with urban discharge, and these contaminants have been detected in fish tissues in San Francisco Bay, although there is little research on PCB levels in the Delta.

Wastewater discharges from WWTPs also are associated with urban and suburban land use. Wastewater contains high levels of nutrients, and the concentrations in effluent are dependent on the level of the treatment system. In the Delta, ammonia historically has been problematic in both the Sacramento and San Joaquin Rivers; however, planned and functioning upgrades to WWTPs have resulted or will result in reductions in ammonia (discussed later in this appendix). Both stormwater runoff and effluent from the Sacramento WWTP have been shown to contain pesticides, including pyrethroids (Weston et al. 2010). Although this will be discussed further, it should be noted that the north Delta intakes are downstream of the Sacramento WWTP discharge and would not affect dilution of effluent.

Endocrine-disrupting compounds (EDCs), which include many of the pesticides, are also referred to as *emerging contaminants* and also are found in urban runoff and wastewater discharges. EDCs include many different types of chemicals from a wide range of sources with widely varying chemical attributes, and their distribution in the Delta is not yet fully understood.

The environmental toxins discussed in this appendix were selected based both on land use discussed above and on other literature that identifies primary constituents of concern to fish in the Delta. The U.S. Environmental Protection Agency (EPA) identified ammonia, selenium, pesticides, and contaminants of emerging concern (including endocrine disruptors) for more focused evaluation in *Water Quality Challenges in the San Francisco Bay/Sacramento–San Joaquin Delta Estuary* (U.S. Environmental Protection Agency 2011). Toxins of concern also are identified under the Clean Water Act Section 303(d) list provided in Table D-3. Those for which total maximum daily load (TMDL) studies have been completed are listed in Table D-4. These lists identify the same toxins listed above plus furans, dioxins, PCBs, mercury/methylmercury, and pathogens. Dioxin, furans, and pathogens are listed only for Stockton, and *E. coli* (a pathogen) is listed for the east Delta.

#### 1 Table D-3. Clean Water Act 2010 Section 303(d) Listed Pollutants and Sources in the Plan Area

Pollutant/Stressor	Listing Region	Listed Source	Delta Location of Listing
Chlordane	Central Valley	Agriculture, Nonpoint Source	N, W
Chlorpyrifos	Central Valley	Agriculture, Urban Runoff/Storm Sewers	N, S, E, W, NW, C, Exp, Stk
DDT	Central Valley	Agriculture, Nonpoint Source	N, S, E, W, NW, C, Exp, Stk
Diazinon	Central Valley	Agriculture, Urban Runoff/Storm Sewers	N, S, E, W, NW, C, Exp, Stk
Dioxin Compounds	Central Valley	Source Unknown, Atmospheric Deposition	Stk
E. Coli	Central Valley	Source Unknown	Е
Invasive Species	Central Valley	Source Unknown, Ballast Water	N, S, E, W, NW, C, Exp, Stk
Furan Compounds	Central Valley	Contaminated Sediments, Atmospheric Deposition	Stk
Group A Pesticides <sup>a</sup>	Central Valley	Agriculture	N, S, E, W, NW, C, Exp, Stk
Mercury	Central Valley	Resource Extraction	N, S, E, W, NW, C, Exp, Stk
Pathogens	Central Valley	Recreational and Tourism Activities (non-boating), Urban Runoff/Storm Sewers	Stk
PCBs	Central Valley	Source Unknown	N, Stk
Unknown Toxicity <sup>b</sup>	Central Valley	Source Unknown	N, S, E, W, NW, C, Exp, Stk
Electrical Conductivity	Central Valley	Agriculture	S, W, NW, Stk
Organic Enrichment/ Low Dissolved Oxygen	Central Valley	Municipal Point Sources, Urban Runoff/Storm Sewers	Stk
Sediment Toxicity	Central Valley	Agriculture	Е
Total Dissolved Solids	Central Valley		S

#### Source:

<a href="http://www.waterboards.ca.gov/water\_issues/programs/tmdl/2010state\_ir\_reports/category5\_report.sht">http://www.waterboards.ca.gov/water\_issues/programs/tmdl/2010state\_ir\_reports/category5\_report.sht</a> ml>. Accessed: November 16, 2011.

DDT = dichlorodiphenyltrichloroethane, PCB = polychlorinated biphenyls.

Delta Locations: C = central, E = east, Exp = export area, N = north, NW = northwest, S = south, STK = Stockton Deep Water Ship Channel, W = west.

- Group A pesticides include aldrin, dieldrin, chlordane, endrin, heptachlor, heptachlor epoxide, BHC (including lindane), endosulfan, and toxaphene.
- b Toxicity is known to occur, but the constituent(s) causing toxicity is unknown.

#### 1 Table D-4. Summary of Completed and Ongoing Total Maximum Daily Loads in the Delta

Pollutant/Stressor	Water Bodies Addressed	Total Maximum Daily Load Status
Chlorpyrifos and Diazinon	Sacramento County urban creeks	TMDL report completed—September 2004
		State-federal approval—November 2004
	Sacramento and San Joaquin	TMDL report completed—June 2006
	Rivers and Delta	State-federal approval—October 2007
	Sacramento and Feather Rivers	TMDL report completed—May 2007
		State-federal approval—August 2008
	Lower San Joaquin River	TMDL report completed—October 2005
		State-federal approval—December 2006
Methylmercury	Delta	TMDL report completed—April 2010
Pathogens	Five-Mile Slough, Lower	TMDL report completed—March 2008
	Calaveras River, Mormon Slough,	State-federal approval—May 2008
	Mosher Slough, Smith Canal, and Walker Slough	
Pesticides	Central Valley	Ongoing
Organochlorine Pesticides	Central Valley	Ongoing
Salt and Boron	Lower San Joaquin River	TMDL report completed—October 2005
		State-federal approval—February 2007
Selenium	San Joaquin River	TMDL report completed—August 2001
		State-federal approval—March 2002
Low Dissolved Oxygen	Stockton Deep Water Ship	TMDL report completed—February 2005
	Channel	State-federal approval—January 2007
Source: <http: td="" www.swrcb.c<=""><td>ca.gov/water_issues/programs/tmc</td><td>dl/#rb5&gt;. Accessed: November 17, 2011.</td></http:>	ca.gov/water_issues/programs/tmc	dl/#rb5>. Accessed: November 17, 2011.
	Channel	State-federal approval—January 20

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The environmental toxins evaluated in this appendix were selected based on historical and current land use along with published literature regarding water quality in the Delta and the types of toxins that have effects on fish.

- 7 

  Selenium
- 8 Copper
- 9 ammonia/um
- 10 Pesticides
- 11 Pyrethroids
- 12 Organochlorines
- 13 Organophosphates

## D.4 Methods

To evaluate effects on covered species, published data on occurrence, biogeochemical behavior, mass balances, quantitative modeling tools, and studies of impacts of specific toxic constituents on covered fish species were reviewed. There are a broad range of available studies specific to the Central Valley and Delta region, many of which are referenced in this appendix. The objective of the analysis in this appendix is to provide an overview of how these constituents could become more bioavailable to covered fish species in the Plan Area and whether there is potential for preliminary proposal actions to result in effects on covered species.

A qualitative framework or conceptual model is presented to evaluate the potential effects of BDCP conservation measures on toxins in the Delta environment, and the possible effects on covered fish species. The effects on covered fish species are dependent more on the increase in both bioavailability and concentration of a given toxin than on just the increase in concentration of the toxin in the water. Given the currently available analytical tools, available occurrence data, and the breadth of the Plan Area, a purely quantitative approach is unable to capture the environmental/chemical factors that result in transformation of a chemical to a form that is more bioavailable and toxic in the ecosystem. Where available field data and quantitative modeling tools were deemed sufficient to capture the relevant aspects of the constituent in estimating impacts, quantitative model results are presented along with a full discussion of the conceptual model for each constituent. Where quantification would lead to results with very high margins of error and uncertainty and would not appropriately inform or define the effects on covered species, effects were discussed only qualitatively with the objective of determining the probability of effects on covered species.

For reference, the EPA Ambient Water Quality Criteria (AWQC) for chronic exposures (AWQC-Fresh Water-Chronic) are included in the discussions of each toxin for context. The AWQC-Fresh Water-Chronic is expressed as the highest concentration of a substance in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect. It should be emphasized that the role of the effects analysis is to evaluate effects on covered species, and not compliance with the Clean Water Act, Basin Plans, or other regulatory guidelines. However, ecological benchmarks are provided where they are useful in evaluating effects.

Presented below is a more detailed description of the components that were examined to develop the qualitative conceptual models, and the quantitative tools that were used to more fully describe the potential effects of toxins on covered fish species. The models were developed to describe the biogeochemistry that determines how these toxins partition in the aqueous system (to sediment, water, or biota), how they are taken into the foodweb, and the potential effects on the covered fish species.

### D.4.1 Problem Formulation

Historical and current land use in the Delta has resulted in the release of potentially toxic constituents into the environment. The effects of toxic constituents on the Delta ecosystem have been identified as contributing to the POD described by Baxter (2010). Preliminary proposal actions may serve to increase or decrease the presence and effects of the toxic constituents already present in the Delta and are deserving of attention in this effects analysis.

## D.4.2 Conceptual Model

Multiple chemical-specific, environmental, and species-specific factors contribute to determining whether a constituent will cause toxic effects on biota. The general conceptual model outlined below and illustrated in Figure D-1 is intended to provide a framework to evaluate these factors and a full description of the potential for each toxin to affect covered fish species under preliminary proposal actions.

The textual explanations in the following sections are meant to provide definitions of factors included in the conceptual model shown in Figure D-1 and information on how the factors work together to determine the ultimate effects on covered fish species. The conceptual model is meant to summarize and synthesize a complex system that integrates chemical-specific biogeochemistry with site-specific environmental factors and species/life stage-specific physiology.

### D.4.2.1 Conceptual Model Components—Toxin Biogeochemistry

The toxins identified in the Delta environment and the fate and transport of these chemicals, along with the propensity for these chemicals to enter the food chain, are evaluated through analysis of the factors discussed below.

#### D.4.2.1.1 Fate and Transport

The conceptual model for toxins includes a discussion of the biogeochemistry of the chemical and the fate and transport characteristics. The analysis of fate and transport involves identifying the source of the toxin in the Delta, how the constituent is transported and accumulates in the ecosystem, and the chemical properties that cause it to partition to sediment/water/air/biota. This analysis integrates the environmental setting and hydrology to determine how and where the toxin is transported from its source area to other parts of the Delta.

The basic chemical characteristics that determine how a toxin is transported and partitions in the environment include solubility in water, tendency to sorb to particulates, and volatility (tendency to occur as a vapor). A toxin with high water-solubility can migrate dissolved in rivers. Alternatively, metals and some pesticides often have low solubility in water and tend to sorb to particulates and organic carbon, so they typically are found in sediments closer to the source.

Chemicals can be broken down in the environment by chemical or biological processes. The rate of this degradation is measured by a chemical-specific half-life, which is the time it takes for half of the mass to break down. Chemical degradation includes photodegradation, where the toxin is chemically broken down by sunlight. Biological degradation is usually a product of bacterial degradation of organic chemicals.

Water chemistry also affects the fate, transport, partitioning, and bioavailability of a toxin in an aqueous system. Salinity, hardness, temperature, pH, organic carbon, and redox potential (in sediments) influence the form that a chemical will take. In many cases, certain forms of a given toxin (species or ionic state) determine partitioning and the ultimate toxicity. For example, copper is more toxic in the cupric species (2+), than in the cuprous species (1+).

#### D.4.2.1.2 Bioavailability, Bioaccumulation

Bioavailability is a measure of the ability of a toxic to cross the cellular membrane of an organism, to become incorporated in that organism, and to enter the food chain (Semple 2004). Not all toxins are in a form that can be taken up by an organism. Bioavailability is not only chemical-specific, but it also can be specific to the chemical form that a constituent takes. For instance, copper in the 2+ state is more bioavailable than copper in the 1+ state, making the first form much more toxic than the second. Mercury in an organic complex as methylmercury is much more bioavailable and toxic than elemental mercury or mercury complexed with an inorganic compound.

In addition to the availability of the chemical to be taken up by biota, some chemicals are magnified more through the food chain. *Bioaccumulation* often is loosely used interchangeably with the term *biomagnification*. Strictly speaking, bioaccumulation occurs at any one trophic level or in any one species (and age-class) as a pollutant is ingested inside of food items or absorbed from the environment and thereby *accumulates* to some concentration in tissues of organisms at that particular trophic level or in that particular species (and age-class). In contrast, *biomagnification* more properly refers to increases in tissue concentrations of a pollutant as it passes upward through the food chain, from prey to predator, to the topmost, mature predators. In these top predators tissue concentrations may be harmful both to the animal (especially to offspring) and to those that consume it. A common example of a pollutant bioaccumulating and biomagnifying to harmful levels is the buildup of mercury in large game fish such as tuna or striped bass. In summary, bioaccumulation happens within a specific trophic level; biomagnification occurs over multiple trophic levels.

Bioaccumulation is a function of the chemical's specific characteristics and the way that the organism metabolizes the chemical—such as whether it is metabolized and excreted, or stored in fat. Toxins that are bioavailable and lipophilic (tend to accumulate in fatty tissue of an organism and are not very water soluble) typically bioaccumulate at higher rates. If stored, the chemical can biomagnify in the food chain, for example, mercury and some pesticides.

# D.4.2.2 Conceptual Model Components—Effects of Preliminary Proposal Actions on Toxins

For the purposes of this analysis, the BDCP conservation measures are grouped as either water operations or restoration, as depicted on Figure D-1. The mercury mitigation conservation measure also will be discussed within the restoration actions.

The primary concern with the BDCP habitat restoration measures regarding toxins is the potential for mobilizing toxins sequestered in sediments of the newly inundated floodplains and marshes. This appendix provides an overview of what toxins are known to be present in these areas and the biogeochemical behaviors that will determine whether they could be mobilized into the aquatic environment and the food chain by restoration actions.

The greatest potential for effects on toxins related to the preliminary proposal water operations is the potential for changes in dilution and mixing of existing toxins. For instance, certain toxins, such as selenium, are known to be present in the San Joaquin watershed. A change in the proportion of San Joaquin water inputs to the Delta relative to the Sacramento River could result in diminished dilution (and increased concentrations) in the Delta of toxins from the San Joaquin watershed. Reduction of flows in the Sacramento River downstream of north Delta intakes also may result in decreased dilution of toxins in the Delta.

# D.4.2.3 Conceptual Model Components—Effects of Changes in Toxins on Covered Fish Species

The previous steps determine if and where preliminary proposal actions potentially could change the amounts and bioavailability of toxins. This step looks at how these changes could affect covered fish species. The toxic effects of a chemical are determined by how it works on a biochemical level. Some of the types of effects are listed in Figure D-1 under *Toxic Effects*. Toxins can target specific tissues, organs, or organ systems. For example, toxins that affect the neurological, immune, or endocrine systems typically lead to potential effects on behavior, ability to combat disease, and reproduction, respectively. Certain toxins tend to accumulate in particular tissues or organs, such as the fatty tissues, liver, or kidneys; those that accumulate in fatty tissues have a greater potential to bioaccumulate. These factors determine the overall effect of the toxin on the organism, and whether it will affect reproductive, developmental, or adult life stages. Effects of a particular toxic chemical can vary between species, and also between life stages within a species. The conceptual model for this effects analysis considers all these factors.

# D.5 Results—Effects of Preliminary Proposal Conservation Measures on Toxins

## D.5.1 Mercury

## D.5.1.1 Mercury—Location, Environmental Fate, and Transport

Mining operations in the mountains drained by Central Valley tributaries resulted in transport and widespread deposition of mercury into the water and sediments of the Delta ecosystem. Mercury, in the form of the mineral cinnabar, was mined mainly from the Coastal Range. In the Sierra Nevada and Klamath-Trinity Mountains, mercury was used for gold recovery in placer and hardrock mining operations (Alpers and Hunerlach 2000; Alpers et al. 2005). Inorganic mercury was transported with sediment loads by creeks and rivers draining the mountains and became distributed throughout the riverbed, marsh, wetland, and floodplain sediments of the Delta, with highest concentrations in upper tributaries.

The Sacramento River is the primary transport route of methylmercury to the Delta and contributes about 80% of riverborne mercury inputs (Stephenson 2007, Wood 2010). The amounts of methylmercury, or organic mercury, will correspond roughly with these percentages. In the Sacramento River watershed, the highest concentrations of mercury are found in CacheCreek and the Yolo Bypass where Cache Creek terminates. Cache Creek, which drains a former mining area, is the largest contributor of mercury to the Delta, as it drains 2% of the area in the Central Valley and contributes 54% of the mercury (Foe 2008). Methylmercury concentrations decrease significantly (by 30% to 60%) downstream of Rio Vista, where concentrations were at or below 0.05 nanograms per liter (ng/L) (Foe 2003; Woods 2010).

Relative to the Sacramento River, the San Joaquin River is a relatively minor contributor of methylmercury to the Delta. Methylmercury water concentrations in some waters of the San Joaquin watershed are comparable or higher than the Sacramento River, butoverall loading is minor because of the low flows. The Mokelumne-Cosumnes River is the greatest contributor of mercuryin the San Joaquin watershed, but accounts for only 2.1% of the total methylmercury in the Delta, with

an average concentration of 0.17 ng/L (Woods 2010). Marsh Creek, which drains the Mt. Diablo mining area, contributes a small percentage (0.04%) because of its size, but it does have relatively high average concentrations of methylmercury estimated at 0.25 ng/L (Woods 2010). Bear Creek and Mosher Creek, which drain a former mining area, are also high in mercury, with concentrations reported at 0.31 ng/L (Woods 2010). These creeks are also small and contribute a relatively small percentage to the overall mercury budget in the Delta.

For reference, the current Criterion Continuous Concentration (AWQC-Fresh Water-Chronic) for mercury in fresh water is 770 ng/L (0.77 micrograms per liter [ $\mu$ g/L]). The criteria can be applied to total mercury (organic plus inorganic mercury), but they are derived from data for inorganic mercury (III) and therefore should be considered underprotective if a substantial portion of mercury occurs as methylmercury. The Delta is listed on the Clean Water Act Section 303(d) list as an impaired water body for mercury in fish tissues (State Water Resources Control Board 2011). The TMDLs for methylmercury in the Delta and in San Francisco Bay are provided in Table D-5. The TMDL for the Delta was approved recently.

#### Table D-5. Mercury and Methylmercury TMDLs in the Delta and San Francisco Bay

Analyte	CTR <sup>a</sup>	EPA Recommended Criteria <sup>b</sup>	Delta Methylmercury TMDL <sup>c</sup>	San Francisco Bay Mercury TMDL <sup>d</sup>
Mercury (ng/L)	50	770	_	25
Methylmercury (ng/L)	<u></u>	- 1	0.06	_

CTR = California Toxics Rule.

- <sup>a</sup> Criterion for the protection of human health from total recoverable mercury in fresh water (U.S. Environmental Protection Agency 2006c).
- b Criterion for the protection of chronic exposure from total mercury to freshwater aquatic life (U.S. Environmental Protection Agency 2006c).
- <sup>c</sup> The recommended water column TMDL concentration of methylmercury for the protection of fish bioaccumulation (Central Valley Regional Water Quality Control Board 2011).
- d The recommended water column 4-day average TMDL concentration for total mercury (U.S. Environmental Protection Agency 2006c).

The chemistry of mercury in the environment is complex (Figure D2). Elemental mercury and mercury in the form of inorganic compounds have relatively low water solubility and tend to accumulate in soils and sediments. When mercury forms an organic complex called monomethylmercury (commonly referred to as methylmercury) it becomes more water soluble and the toxicity and bioavailability are greatly enhanced, making it a primary concern for ecosystem effects. The toxicity of methylmercury is amplified as it biomagnifies through the foodweb. Because of the widespread presence of toxic methylmercury in the Delta, much recent research has been completed on the cycling of methylmercury through the physical environment and biota of the area. The biogeochemistry of mercury in an aqueous system is illustrated on Figure D-2.

Conversion of inorganic mercury to methylmercury occurs in flooded fine sediments subjected to periodic drying-out periods and is associated with anaerobic (oxygen-depleted), reducing environments (Alpers et al. 2008; Ackerman and Eagles-Smith 2010). Methylmercury production is higher in high marshes that are subjected to wet and dry periods over the highest monthly tidal cycles; production appears to be lower in low marshes that are always inundated and not subject to dry periods (Alpers et al. 2008). Relatively high rates of methylmercury production also have been

attributed to agricultural wetlands, mainly rice fields (Windham-Myers et al. 2010). Numerous other factors affect methylation of mercury in estuarine environments in addition to inundation regime; they include vegetation, grain size, pH, availability of binding constituents (iron, sulfur, organic matter), and factors influencing success of the microbes responsible for the methylation process (nutrients and dissolved oxygen) (Alpers et al. 2008; Wood et al. 2010).

In-situ production of methylmercury in Delta sediments is an important source of this toxin to the Delta ecosystem. Several investigators have quantified inputs of methylmercury to the Delta from sediments, with varying results (Stephenson 2007; Byington 2007; Foe 2008; Wood et al. 2010). Results of the CALFED Mercury Project Annual Report for 2007 (Stephenson 2007) indicate that river inputs (11.5 grams per day [g/day] methylmercury) and in-situ production from wetland/marsh sediments (11.3 g/day methylmercury) are the leading sources of methylmercury to the Delta waters, and have roughly comparable levels of input. Wood (2010) estimates that in-situ methylmercury production in open water and wetlands contributes approximately 36% of the overall methylmercury load to the Delta (approximately 5 g/day) but is less than riverine/tributary inputs (8 g/day). The higher estimate of methylmercury production from sediments reported by Stephenson is based on periods of higher water (wet) and may be more representative of what might occur when new restoration opportunity areas (ROAs) are opened for inundation, especially when combined with the effects of sea level rise.

Despite all sources of methylation, the Delta remains a net sink for waterborne methylmercury, and photodegradation that results in demethylation of mercury may be an important factor in methylmercury losses from the system (Stephenson et al. 2008).

In the methylmercury budgets developed by Woods (2010), Foe (2008), Byington (2007), and Stephenson (2007), photodegradation rates are higher than sediment production rates for methylmercury. Gill (2008) identified photodegradation of methylmercury as potentially the most effective mercury detoxification mechanism in the Delta.

Specific photodegradation rates vary on dailyand monthly timescales, as the process is dependent on light intensity (Gill 2008). Photodegradation of methylmercury occurs in the photic zone of the water column (the depth of water within which natural light penetrates) and as such can be expected to occur in a large portion of the shallow, newly inundated ROAs. At the 1% light level, the mean depth for the photic zone in the Delta was calculated to be 2.6 meters, with measured depths ranging from 1.9 meters to 3.6 meters (Gill 2008; Byington 2007). Gill and Byington also conclude that photodegradation may be most active in the top half-meter of the water column in the Delta.

Mediated by sunlight, photodegradation occurs at higher levels in the dry season than in the wet season, with minimum photodegradation rates occurring December through February and maximum degradation rates occurring in May and June (Byington 2007). Research by Byington indicates that photodegradation of methylmercury in marshes and tules in the Delta is severely diminished by reduced light penetration resulting from the presence of high dissolved organic carbon (DOC), turbidity, and aquatic vegetation.

Atmospheric deposition also may contribute to the mercury load; however, estimated daily loads are an order of magnitude lower than most other sources to the Delta and constitute approximately 1% of the entire methylmercury load contributed from external and in Delta sources (Wood et al. 2010). In addition, atmospheric contributions are not anticipated to be altered by preliminary proposal actions. Therefore, atmospheric deposition can be considered an insignificant source from the perspective of assessing preliminary proposal effects.

# D.5.1.2 Mercury—Effects of Preliminary Proposal Conservation Measures

Quantitative modeling was performed to estimate the effects of preliminary proposal water operations on mercury and methylmercury in the aquatic system and on covered speciesModeling was based on DSM2 output that estimated changes in water flows under preliminary proposed actions. Results were considered in the context of a qualitative discussion to fully capture some of the factors that were not quantified, including mercury methylation in ROAs and biogeochemical factors that affect concentrations, environmental partitioning, degradation, and bioavailability.

#### D.5.1.2.1 Water Operations

#### **Modeling Methods**

Average waterborne methylmercury concentrations are compared to co-located fish tissue mercury concentrations to construct a simple regression model to predict future fish concentrations from water, as was done for the Delta methylmercury TMDL (Central Valley Regional Water Board 2011). In the case of the current study, the model is based on the DSM2-predicted blending of various source waters with known, measured average concentrations of total and methylmercury, and the known relationship between modeled methylmercury and largemouth bass fillet concentrations of mercury. The resulting model allows the prediction of future, altered average fish tissue mercury concentrations under the preliminary proposal water operations. For this modeling effort, largemouth bass was used as the example fish. Although this is not a covered fish species, there are sufficient data to develop relationships between water and fish concentrations, and largemouth bass is a high level consumer relative to the covered fish species and would show effects from bioaccumulation.

The source-water concentrations used in the model are listed in Table D-6. Modeling methods are more fully described in Attachment D.A.



#### Table D-6. Historical Methylmercury Concentrations in the Five Delta Source Waters for the Period 2000–2008

		Source Water									
Data Parameters	Sacramento River*		San Joaqu	San Joaquin River*		San Francisco Bay*		East Side Tributaries*		Agriculture in the Delta*	
Mean (ng/L)	0.10	0.03	0.15	0.03	0.032	(4)	0.22	0.08	0.25	_	
Minimum (ng/L)	0.05	0.03	0.09	0.01			0.02	0.02		_	
Maximum (ng/L)	0.24	0.03	0.26	0.08	_		0.32	0.41		_	
75th Percentile (ng/L)	0.12	0.03	0.18	0.06	-//	_	0.20	0.15	_	_	
99th Percentile (ng/L)	0.23	0.03	0.26	0.08	€ <del>+</del>	V 4	0.31	0.39	_	_	
Data Source		lley Water 2008a	Valley Wa	.0; Central iter Board 08a	SFEI 2010	_		lley Water 2008a	Central Valley Water	-	
				USGS 2010				USGS 2010	Board 2008a		
Station(s)		to River at port	San Joaquin River at Vernalis		Martinez		Mokelumne and Calaveras Rivers		Mid-Delta locations, median		
Date Range	2000- 2003	2000	2000- 2001; 2003- 2004	2000- 2002	2007	\$	2000- 2001; 2003- 2004	2000; 2002	2008	-	
ND Replaced with RL Not Applicable		Not Yes Applicable				Yes		Not Applicable			
Data Omitted	None		None		(- // )		None		None		
No. of Data Points	36	1	49	25	42	[ <b>-</b> / <b>-</b>	27	9		_	

Sources: BDAT Website 2010; Central Valley Regional Water Quality Control Board 2008a; San Francisco Estuary Institute Website 2010; U.S. Geological Survey Website 2010.

#### Notes:

Means are geometric means. ng/L = nanograms per liter.

\* The total recoverable concentration of the analyte is presented in first cell and the dissolved concentration of the analyte is presented in the second column.

#### Modeling Results—Water Operations

Modeling showed small, insignificant changes in total mercury and methylmercury levels in water and fish tissues due to PP water operations.

Under current conditions, total mercury and methylmercury concentrations in water exceed TMDL target values, and PP water operations will not change this condition. Estimated concentrations of mercury in water under EBC2\_ELT and the PP\_ELT are shown in Table D-7 (for total mercury) and Table D-8 (for methylmercury). Estimated concentrations for the late-long-term (LLT) scenario are provided in Table D-10 and Table D-11.

Currently, mercury concentrations in fish tissues exceed Delta TMDL guidance targets, which are set for human health rather than effects on fish, and the PP is not expected to substantially alter this condition through water operations. Modeled concentrations of total mercury in fish are presented in Table D-9 and Table D-12.

#### Table D-7. Modeled Mercury Concentrations in Water: Early Long-Term

		Period Average Concentration (μg/L)					
		Existing Conditions					
Location	Period*	(EBC2)	EBC2_ELT	PP_ELT			
Delta Interior							
Mokelumne River at Staten Island	All	0.0052	0.0052	0.0054			
	Drought	0,0046	0.0047	0.0048			
San Joaquin River at Buckley Cove	All	0.0075	0.0076	0.0075			
	Drought	0.0073	0.0075	0.0074			
Old River at Rancho del Rio	All	0.0051	0.0051	0.0052			
	Drought	0.0046	0.0046	0.0045			
Western Delta		- market					
Sacramento River above Pt. Sacramento	All	0.0044	0.0044	0.0045			
	Drought	0.0044	0.0045	0.0045			
San Joaquin River at Antioch Ship	All	0.0050	0.0051	0.0052			
Channel	Drought	0.0049	0.0050	0.0049			
Sacramento River at Mallard Island	All	0.0056	0.0056	0.0058			
	Drought	0.0058	0.0059	0.0059			
	Drought	0.0058	0.0060	0.0057			

#### Notes:

The recommended water column 4-day average TMDL concentration for total mercury =  $0.025~\mu g/L$ . (U.S. Environmental Protection Agency 2006c.)

These data are preliminary and are subject to change as BDCP analyses are finalized.

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<sup>\*</sup> All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of drought and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).

#### 1 Table D-8. Modeled Methylmercury Concentrations in Water: Early Long-Term

		Period Average Concentration (μg/L)			
Location	Period*	Existing Conditions (EBC2)	EBC2_ELT	PP_ELT	
Delta Interior					
Mokelumne River at Staten Island	All	0.000136	0.000135	0.000145	
	Drought	0.000122	0.000122	0.000127	
San Joaquin River at Buckley Cove	All	0.000159	0.000164	0.000166	
	Drought	0.000161	0.000168	0.000172	
Old River at Rancho del Rio	All	0.000122	0.000122	0.000124	
	Drought	0.000113	0.000114	0.000115	
Western Delta	•				
Sacramento River above Pt. Sacramento	All	0.000103	0.000103	0.000104	
	Drought	0.000101	0.000101	0.000101	
San Joaquin River at Antioch Ship	All	0.000104	0.000103	0.000105	
Channel	Drought	0.000094	0.000093	0.000094	
Sacramento River at Mallard Island	All	0.000083	0.000083	0.000083	
	Drought	0.000073	0.000072	0.000072	
	Drought	0.000135	0.000136	0.000133	

#### Notes:

The recommended water column TMDL concentration of methylmercury for the protection of fish bioaccumulation = 0.06 ng/L (.00006  $\mu$ g/L). (Central Valley Regional Water Quality Control Board 2008a.) Exceedances are shaded and in italics.

These data are preliminary and are subject to change as BDCP analyses are finalized.

<sup>\*</sup> All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of drought and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).

#### 1 Table D-9. Modeled Mercury Concentrations in Largemouth Bass Fillets: Early Long-Term

		ELT Period Average Largemouth Bass Fillet Mercury Concentrations (mg/kg ww)			
Location	Period*	Existing Conditions (EBC2)	EBC2_ELT	PP_ELT	
	Delta I	nterior			
Mokelumne River at Staten Island	All	0.521	0.516	0.561	
	Drought	0.459	0.459	0.481	
San Joaquin River at Buckley Cove	All	0.624	0.647	0.656	
	Drought	0.633	0.666	0.684	
Old River at Rancho del Rio	All	0.459	0.459	0.467	
	Drought	0.420	0.424	0.428	
Western Delta					
Sacramento River above Pt. Sacramento	All	0.377	0.377	0.381	
	Drought	0.368	0.368	0.368	
San Joaquin River at Antioch Ship	All	0.381	0.377	0.385	
Channel	Drought	0.339	0.334	0.339	
Sacramento River at Mallard Island	All	0.293	0.293	0.293	
	Drought	0.252	0.248	0.248	

#### Notes:

Fish tissue concentrations were evaluated in relation to the Delta methylmercury TMDL tissue targets of 0.24 mg mercury/kg wet-weight of largemouth bass fillets (muscle tissue) for fish normalized to a standard 350 mm total length (Central Valley Regional Water Quality Control Board 2008a). Exceedances are shaded and in italics.

<sup>\*</sup> All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5–consecutive year (water years 1987–1991) drought period consisting of drought and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index). These data are preliminary and are subject to change as BDCP analyses are finalized.

#### 1 Table D-10. Modeled Mercury Concentrations in Water: Late Long-Term

		Period Average Concentration (μg/L)			
Location	Period*	Existing Conditions (EBC)	EBC2_LLT	PP_LLT	
Delta Interior			•		
Mokelumne River at Staten Island	All	0.0052	0.0051	0.0053	
	Drought	0.0046	0.0046	0.0047	
San Joaquin River at Buckley Cove	All	0.0075	0.0075	0.0075	
	Drought	0.0073	0.0073	0.0074	
Old River at Rancho del Rio	All	0.0051	0.0051	0.0053	
	Drought	0.0046	0.0046	0.0047	
Western Delta	•				
Sacramento River above Pt. Sacramento	All	0.0044	0.0045	0.0045	
	Drought	0.0044	0.0045	0.0045	
San Joaquin River at Antioch Ship	All	0.0050	0.0050	0.0052	
Channel	Drought	0.0049	0.0049	0.0049	
Sacramento River at Mallard Island	All	0.0056	0.0056	0.0058	
	Drought	0.0058	0.0059	0.0059	
	Drought	0.0058	0.0060	0.0058	

#### Notes:

The recommended water column 4-day average TMDL concentration for total mercury =  $0.025~\mu g/L$ . (U.S. Environmental Protection Agency 2006c.) Exceedances are shaded and in italics.

These data are preliminary and are subject to change as BDCP analyses are finalized.

<sup>\*</sup> All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of drought and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).

#### 1 Table D-11. Modeled Methylmercury Concentrations in Water: Late Long-Term

		Period Average Concentration (μg/L)			
Location	Period*	EBC	EBC2_LLT	PP_LLT	
Delta Interior			•		
Mokelumne River at Staten Island	All	0.000136	0.000134	0.000142	
	Drought	0.000122	0.000121	0.000126	
San Joaquin River at Buckley Cove	All	0.000159	0.000164	0.000162	
	Drought	0.000161	0.000168	0.000167	
Old River at Rancho del Rio	All	0.000122	0.000123	0.000126	
	Drought	0.000113	0.000116	0.000118	
Western Delta	· ·				
Sacramento River above Pt. Sacramento	All	0.000103	0.000103	0.000103	
	Drought	0.000101	0.000101	0.000100	
San Joaquin River at Antioch Ship	All	0.000104	0.000103	0.000105	
Channel	Drought	0.000094	0.000094	0.000094	
Sacramento River at Mallard Island	All	0.000083	0.000083	0.000082	
	Drought	0.000073	0.000073	0.000072	
	Drought	0.000135	0.000138	0.000136	

#### Notes

The recommended water column TMDL concentration of methylmercury for the protection of fish bioaccumulation = 0.06 ng/L (0.00006 µg/L). (Central Valley Regional Water Quality Control Board 2008a.) Exceedances are shaded an in italics.

<sup>\*</sup> All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of drought and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).

These data are preliminary and are subject to change as BDCP analyses are finalized.

#### 1 Table D-12. Modeled Mercury Concentrations in Largemouth Bass Fillets: Late Long-Term

	Period*	LLT Period Average Largemouth Bass Fillet Mercury Concentration (mg/kg ww)			
Location		EBC	EBC2_LLT	PP_LLT	
Delta Interior		•			
Mokelumne River at Staten Island	All	0.521	0.512	0.547	
	Drought	0.459	0.454	0.476	
San Joaquin River at Buckley Cove	All	0.624	0.647	0.638	
	Drought	0.633	0.666	0.661	
Old River at Rancho del Rio	All	0.459	0.463	0.476	
	Drought	0.420	0.433	0.441	
Western Delta	•				
Sacramento River above Pt. Sacramento	All	0.377	0.377	0.377	
	Drought	0.368	0.368	0.364	
San Joaquin River at Antioch Ship	All	0.381	0.377	0.385	
Channel	Drought	0.339	0.339	0.339	
Sacramento River at Mallard Island	All	0.293	0.293	0.289	
	Drought	0.252	0.252	0.248	

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Fish tissue concentrations were evaluated in relation to the Delta methylmercury TMDL tissue targets of 0.24 mg mercury/kg wet-weight of largemouth bass fillets (muscle tissue) for fish normalized to a standard 350 mm total length (Central Valley Regional Water Quality Control Board 2008a). Exceedances are shaded an in italics.

#### **Uncertainty Analysis**

The model captures effects due to preliminary proposal water operations but does not estimate the potential for methylation in existing or newly created environments (e.g., ROAs). The detailed, site-specific information needed to construct such a model, with acceptable margins of error, is lacking but may be developed as part of specific, future evaluations of actions (see discussion above concerning key processes controlling mercury fate, transport, and risk determination). Agricultural and existing wetlands may be very different in production of methylmercury and uptake into various trophic levels and are not easily generalized or modeled (Windham-Myers et al. 2010).

#### D.5.1.2.2 Restoration

As discussed above, in-situ conversion of mercury to methylmercury occurs at highest rates in intermittently flooded marshes and floodplains, as well as flooded agricultural areas. Preliminary proposal restoration actions will expand intermittently wetted areas by converting managed marshes, diked wetlands, agricultural areas, and other upland areas to tidal, open-water, and floodplain habitats (see Chapter 3, *Conservation Strategy*, for details of restoration), resulting in new areas with the potential to increase methylmercury in the aquatic system.

<sup>\*</sup> All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of drought and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index). These data are preliminary and are subject to change as BDCP analyses are finalized.

Woods and coauthors (2010) estimated rates of methylmercury generation for intertidal and floodplain areas (0.0369 g/acre/year) and for open-water production (0.01476 g/acre/year).

However, methylmercury generation rates ultimately aredependent on the concentrations of mercury in the soils and on the specific biogeochemistry of the system. For this effects analysis, the margin of error on applying these estimated production rates across a wide geographic area with varying hydrology and concentrations of sequestered mercury was deemed to be too large to produce a reliable estimate of methylmercury generation at the scale of the ROAs.

The Sacramento River watershed, and specifically the Yolo Bypass, is the primary source of mercury in the Delta. The highest concentrations of mercury and methylmercury are in the Cache Creek area and the Yolo Bypass. The amount of methylmercury produced in the Yolo Bypass has been estimated to represent 40% of the total methylmercury production for the entire Sacramento watershed (Foe et al. 2008). Water discharging from the Yolo Bypass at Prospect Slough has a reported average annual methylmercury concentration of 0.27 ng/L, compared to the 0.06 ng/L TMDL (set for human health from bioaccumulation effects in fish).

The highest levels of methylmercury generation, mobilization, and bioavailability are expected in the Yolo Bypass, which will be subjected to more frequent and wider areas of inundation under the preliminary proposal actions. The concentrations of methylmercury in water exiting the Yolo Bypass will depend on many variables. Recent studies in the Yolo Wildlife Management Area showed that methylmercury increased with increased flow rates and increased residence time (Windham-Myer 2010). This same study also noted that the residence time in Cache Settling Basin, seasonality, and agricultural practices all factor into methylmercury production and cycling through the system in the Yolo Bypass. Marvin-DiPasquale and coauthors (2009) also identified a wide range of site-specific factors that determine methylmercury production, as well as variability in distribution and speciation of mercury in wetlands in the Yolo Bypass. Foe and coauthors (2008) developed an empirical relationship between net methylmercury production in the Yolo Bypass and outflow (methylmercury production =  $0.0042*(flow)^{0.782}$ ), but given the varied factors controlling methylmercury cycling, this calculation will not provide an estimate of methylmercury production in the Yolo Bypass that can be relied on with any certainty.

The preliminary proposal for the Yolo Bypass has the potential to increase the loading, concentrations, and bioavailability of methylmercury in the aquatic system in the Yolo Bypass. Currently, the methylmercury in water discharging from the Yolo Bypass to the Sacramento River is 0.27 ng/L (annual average) (Foe et al. 2008). This concentration likely will increase under the preliminary proposal, but will be mitigated to some extent by CM12, as discussed below. The current and future concentrations of methylmercury will exceed the TMDL (set for human health from bioaccumulation effects in fish) concentration of 0.06 ng/L. Also, decreased flows in the Sacramento River due to preliminary proposal upstream water operations may reduce the dilution capacity of the Sacramento River and result in increased concentrations of methylmercury in the river.

As part of the preliminary proposal, measures will be implemented to mitigate the production of methylmercury in ROAs. These measures may include construction and grading that minimize exposure of mercury-containing soils to the water column, design to support photodegradation, and pre-design field studies to identify depositional areas where mercury accumulation is most likely and characterization and/or design that avoids these areas. Recent studies performed by Heim with others (in press) indicate that integrating permanent ponds into restoration designs may reduce mercury methylation and mobilization. CM12 provides for consideration of new information as it develops that could effectively minimize methylmercury production and mobilization. Also, the

1	Delta TMDL	for methylmercury v	vas adopted recently ((	Central Valley Regional	Water Quality
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- 2 Control Board 2011) and will be integrated into the overall preliminary proposal through CM12
- 3 (discussed below) and adaptive management.
- 4 Photodegradation may be an important factor in reducing methylmercury generation, and design to
- 5 enhance photodegradation has been included in CM12. Recent research has indicated that
- 6 photodegradation of methylmercury in shallow waters can remove an amount of methylmercury
- 7 similar to that produced in sediments of the Delta system (Byington 2008). Photodegradation has
- 8 high potential to remove a percentage of the methylmercury produced in newly restored areas, with
- 9 the rates partially dependent on the turbidity of the water column and the resultant depth of the
- photic zone. However, demethylation by photodegradation still leaves the less toxic inorganic
- mercury in the system. More research into the fate of mercury following photodegradation is
- 12 needed.
- As discussed throughout this section, the biogeochemistry and fate and transport of mercury and
- methylmercury are very complex. Restoration will involve inundation of areas where mercury has
- been sequestered in soils, and if methylation occurs, the methylmercury will be mobilized into the
- aquatic system. Once in the aquatic system, the methylmercury can be transported with water flow,
- taken up by biota, volatilized, demethylated, and returned to sediment (but not necessarily at the
- original restoration site). As a result of these processes, the mercury may be transported away from
- the restoration site, resulting in an overall decrease of mercury in the soils, which will reduce the
- source at the ROA. Based on this conceptual model, the mercury available for methylation at the
- 21 ROA may decrease over time. However, the length of time for this to be quantifiable is not known.

### 22 **D.5.1.2.3** Mercury Summary

- 23 Preliminary proposal restoration actions are likely to result in increased production, mobilization,
- and bioavailability of methylmercury in the aquatic system. Modeling of water operations effects
- showed little changes in methylmercury concentrations in water or fish tissue, although
- 26 methylmercury concentrations in both media would continue to exceed criteria under the
- 27 preliminary proposal.
- 28 Methylmercury likely would be generated by inundation of restoration areas, with highest
- 29 concentrations expected in the Yolo Bypass, Cosumnes and Mokelumne Rivers, and at other ROAs
- 30 closest to these source areas.
- 31 CM12 Methylmercury Management will help to minimize the increased mobilization of
- 32 methylmercury at restoration areas. It describes pre-design characterization, design elements, and
- 33 best management practices to mitigate methylation of mercury, and requires monitoring and
- reporting of observed methylmercury levels.

### D.5.2 Selenium

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### D.5.2.1 Selenium—Location, Environmental Fate, and Transport

- 37 Selenium is a naturally occurring micronutrient that can have significant ecological effects at
- 38 elevated concentrations. Selenium has been identified as an important toxin in the Delta, especially
- in the San Joaquin watershed where irrigation practices mobilize naturally occurring selenium from
- 40 the soils. In the Delta watershed, selenium is most enriched in marine sedimentary rocks of the
- 41 Coast Ranges on the western side of the San Joaquin Valley (Presser and Piper 1998). Irrigation of

soils derived from the marine rocks leaches the selenium, and the subsequent practice by farmers to drain excess shallow groundwater from the root zone to protect their crops results in elevated concentrations of selenium in groundwater and receiving rivers (McCarthy and Grober 2001).

For reference, the current AWQC-Fresh Water-Chronic for selenium in fresh water is  $5.0~\mu g/L$  and is expressed as the total recoverable metal in the water column. In the Grassland waterways and Salt Slough, a more protective chronic value of  $2~\mu g/L$  applies, in consideration of sensitive listed species. The lentic conditions of water in the marshes were also a factor in setting these site-specific objectives. Available criteria, standards, and objectives for selenium are presented in Table D-13.

# Table D-13. Applicable Federal Criteria, State Standards/Objectives, and Other Relevant Effect Thresholds for Selenium

	Region 5 Basin Plan <sup>a</sup>	Region 2 Basin Plan <sup>b</sup>	CTR <sup>c</sup>	Drinking Water MCL <sup>d</sup>	EPA Recommended Criteria <sup>e</sup>	Other Relevant Thresholds <sup>f</sup>
Selenium (µg/L)	5/12	5/20	5/20	50	5/variable	2

- Objectives apply to the lower San Joaquin River from the mouth of the Merced River to Vernalis as  $5 \mu g/L$  (4-day average) and  $12 \mu g/L$  (maximum concentration) total selenium concentration (Central Valley Regional Water Quality Control Board 2009a).
- <sup>b</sup> Selenium criteria were promulgated as total recoverable concentrations for all San Francisco Bay/Delta waters in the National Toxics Rule (NTR) (U.S. Environmental Protection Agency 1992; San Francisco Bay Regional Water Quality Control Board 2007).
- <sup>c</sup> Standard is Criterion Continuous Concentration as  $5 \mu g/L$  total recoverable selenium; California Toxics Rule (CTR) deferred to the NTR for San Francisco Bay/Delta waters and San Joaquin River (U.S. Environmental Protection Agency 2000).
- $^{\rm d}$  In addition, the California Office of Environmental Health Hazard Assessment (2010) has recommended a Public Health Goal of 30  $\mu g/L$
- <sup>e</sup> Criteria for protection of freshwater aquatic life are 5 μg/L (continuous concentration, 4-day average) total recoverable selenium and they vary for the Criterion Maximum Concentration (CMC) (24-hour average) (U.S. Environmental Protection Agency 2010). The CMC = 1/[[f1/CMC1] + (f2/CMC2)] where f1 and f2 are the fractions of total selenium that are treated as selenite and selenate, respectively.
- f Concentration as total recoverable selenium identified as a Level of Concern for the Grassland Bypass Project (Beckon et al. 2008) and the site-specific objective for the Grassland (Central Valley Regional Water Quality Control Board 1996).

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It should be noted that in addition to the adopted water quality objectives shown here, at the national level, EPA plans to propose Clean Water Act Section 304(a) selenium guidance criteria for aquatic life for freshwater chronic values only, and will distinguish between flowing and standing waters (U.S. Environmental Protection Agency 2011). These guidance criteria will form the basis for adopting protective water quality standards expressed as tissue concentration of selenium in fish egg or ovary and a corresponding water column concentration, where tissue concentration data are not available. Concentrations in tissue, such as bird eggs or fish tissue, better indicate actual exposure and, in combination with foodweb information, provide a basis for deriving site-specific numeric water column values. The revised national guidance criteria will be supplemented by regional efforts. EPA Region 9, in conjunction with the U.S. Geological Survey (USGS), U.S. Fish and Wildlife Service (USFWS), and National Marine Fisheries Service (NMFS) and pursuant to its obligations under the Endangered Species Act, is developing criteria to protect threatened and endangered wildlife species, aquatic-dependent species, and aquatic life in California. The first phase of this effort addresses San Francisco Bay and the Delta. It uses data on affected species and relies on

the Presser-Luoma (2010) ecosystem-based model, a model that accounts for foodweb processes and site-specific conditions. This phase is scheduled for completion in 2011, followed by a second phase for statewide criteria (including the San Joaquin River and its tributaries).

Selenium is highly bioaccumulative and can cause chronic toxicity (especially impaired reproduction) in fish and aquatic birds (Ohlendorf 2003; San Francisco Bay Regional Water Quality Control Board 2009). Developmental effects on fish from selenium are well-documented; locally, significant ecosystem effects were described in the early 1980s from water management practices that discharged groundwater containing selenium to the Kesterson Reservoir in the San Joaquin Valley, California. The fate and transport section below provides an overview of selenium sources in the Delta, and the biogeochemical processes that result in increased bioavailability of selenium in an aqueous system. The discussion focuses on the San Joaquin watershed and how selenium could be mobilized by preliminary proposal actions.

The main controllable sources of selenium in the Bay-Delta estuary are agricultural drainage (generated by irrigation of seleniferous soils in the western side of the San Joaquin basin) and discharges from North Bay refineries (in processing selenium-rich crude oil). Both the San Joaquin River and North Bay selenium loads have declined in the last 15 years in response to, first, a control program in the San Joaquin Grassland area, and, second, National Pollutant Discharge Elimination System (NPDES) permit requirements established for refineries in the late 1990s. The annual loads of selenium (mostly as selenate) entering the Bay-Delta estuary from the San Joaquin and Sacramento Rivers vary by water year (that is, by flow), but dissolved selenium loadings averaged 2,380 kg/year from the San Joaquin and 1,630 kg/year from the Sacramento in the 1990–2007 period. The Sacramento River selenium concentration, however, is essentially at background levels (.06 +/-.02  $\mu$ /L), without evidence of significant controllable sources (U.S. Environmental Protection Agency 2011).

The San Joaquin watershed, and specifically the Grassland section of the watershed, historically has been identified as a source of selenium to the Delta. However, mitigation measures have been put into place to manage selenium discharges to meet regulatory requirements. According to the Grassland Project Report for 2006–2007, selenium loads already had been reduced by 75% in 2007 relative to 1996 levels (San Francisco Estuary Institute for the Oversight of the Grassland Project Subcommittee—Chapter 2, 2006–2007). Concentrations of selenium in Salt Slough reportedly met the monthly mean goal of 2  $\mu$ g/L (U.S. Environmental Protection Agency 2011b). Selenium concentrations measured in the San Joaquin River were consistently below 5  $\mu$ g/L (San Francisco Estuary Institute for the Oversight of the Grassland Project Subcommittee—Chapter 2, 2006–2007). As selenium discharge from the Grassland continues to decrease as the 5  $\mu$ g/L goal is approached, concentrations in the San Joaquin River also can be expected to decrease.

Under the Grassland Bypass Project, selenium discharges to Mud Slough (in the San Joaquin watershed) must be reduced to 5  $\mu$ g/L (4-day average) by December 31, 2019. Further, the Central Valley Regional Water Quality Control Board (2010a) recently approved an amendment to the basin plan in light of this project. The amendment requires that agricultural drainage be halted after December 31, 2019, unless water quality objectives are met in Mud Slough (north) and the San Joaquin River between Mud Slough (north) and the mouth of the Merced River. Also, if the State Water Resources Control Board (State Water Board) finds that timely and adequate mitigation is not being implemented, it can prohibit discharge any time before December 31, 2019. As a result, a substantial reduction in selenium inputs (unrelated to the preliminary proposal) to the San Joaquin

River by 2019 would be expected to result in lower selenium inputs to the Delta from the San Joaquin River.

Elevated selenium concentrations also have been identified in Suisun Bay. Although particulate concentrations of selenium (the most bioavailable) in this region are considered low, typically between 0.5 and 1.5 micrograms per gram ( $\mu$ g/g), the bivalve *C. amurensis* contains elevated levels of selenium that range from 5 to 20  $\mu$ g/g (Stewart 2004). Given the fact that *C. amurensis* may occur in abundances of up to 50,000 per m², this area can be considered a sink for selenium because 95% of the biota in some areas are made up of this clam.

Selenium can occur in four oxidation stages as selenates ( $Se^{6+}$ ), selenites ( $Se^{4+}$ ), selenides ( $Se^{2-}$ ), and elemental selenium. The oxidized state, selenates ( $Se^{6+}$ ), is soluble and the predominant species in alkaline surface waters and oxidizing soil conditions. Selenates are readily reduced to selenites ( $Se^{4+}$ ) and selenides ( $Se^{2-}$ ), which are more bioavailable than selenate. Further reduction to elemental selenium can result in an insoluble precipitate, which is not bioavailable.

Although selenium is soluble in an oxidized state, the majority typically becomes reduced and partitions into the sediment/particulate phases in an aqueous system; these reduced sediment/particulate phases are the most bioavailable (Presser and Luoma 2010). Selenium in soils is taken up by plant roots and microbes and enters the food chain through uptake by lower organisms. A portion of the selenium also is recycled into sediments as biological detritus. Lemly and Smith (1987) indicate that up to 90% of the total selenium in an aquatic system may be in the upper few centimeters of sediment and overlying detritus (Lemly 1998).

Oxidized forms of selenium (selenates and selenites) may reduce further to precipitate as elemental selenium or complex with particulates. Selenate reduces to elemental selenium through dissimilatory reduction through reactions with bacteria. These reactions reduce selenium from surface waters, resulting in an increase in selenium concentrations in sediment over time. In wetlands in particular, the organic-rich stagnant waters create a chemically reducing environment in which dissolved selenate is able to convert to selenite or elemental selenium (Werner et al. 2008). The longer the residence time of surface waters, the higher the particulate concentration resulting in higher selenium concentrations in wetlands and shallows (Presser and Luoma 2006). Aquatic systems in shallow, slow-moving water with low flushing rates are thought to accumulate selenium most efficiently (Presser and Luoma 2006; Lemly 1998). However, the ratio of selenium in particulates (which is more bioavailable) to selenium in the water column is a complex relationship that can vary across different hydrologic regimes and seasons (Presser and Luoma 2010).

Because bioaccumulation can be an important component of selenium toxicity, water column selenium concentrations are not reliable indicators of risk to biota (Presser and Luoma 2010). Selenium enters the food chain at a low trophic level and, under certain conditions, is magnified up the food chain. Lower trophic organisms can bioaccumulate hundreds of times the waterborne concentration of selenium, especially where a food chain is based on sessile filter feeders. However, research has demonstrated that bioaccumulation is less important when the food chain is based on plankton rather than on sessile filter feeders, because plankton excrete most of the selenium they consume (Stewart 2004). This is an important factor that mitigates bioaccumulation in some of the preliminary proposal covered fish species, and is more fully discussed in later sections of this appendix.

# D.5.2.2 Selenium—Effects of Preliminary Proposal Conservation Measures

Because the San Joaquin River historically has been a major contributor of selenium to the Delta system, there is concern that the increased contribution to the Delta from the San Joaquin River relative to the Sacramento River as a result of preliminary proposal operations would result in an increase in selenium transport and bioaccumulation in the Delta.

Quantitative modeling was performed to estimate the effects of preliminary proposal water operations on selenium in the aquatic system and on covered fish species. Modeling was based on DSM2 output that estimated changes in water flows under the preliminary proposed actions, and estimated selenium concentrations in source waters that discharge into the Delta. Results were considered in the context of a qualitative discussion to fully capture some of the factors that were not quantified.

### D.5.2.2.1 Water Operations

#### Modeling Methods

Quantitative models were used to estimate the concentrations of selenium in the water column and expected resultant concentrations of selenium in fish tissue. Modeling methods for estimating selenium concentrations in water and in fish tissue for EBC, EBC2\_ELT/LLT and PP\_ELT/LLT are described in Attachment D.B to this appendix. The modeling is based on water and fish tissue sample data and DSM2 model results, and provides an analysis of the effects of preliminary proposal water operations on selenium concentrations.

The output from the DSM2 model (expressed as percent inflow from different sources) was used in combination with the available measured waterborne selenium concentrations to model concentrations of selenium at locations throughout the Delta. These modeled waterborne selenium concentrations were used in the relationship model to estimate bioaccumulation of selenium in whole-body fish and bird eggs. Selenium concentrations in fish fillets then were estimated from those in whole-body fish.

Selenium concentrations in whole-body fish and bird eggs were calculated using ecosystem-scale models developed by Presser and Luoma (2010). The models were developed using biogeochemical and physiological factors from laboratory and field studies; information on loading, speciation, and transformation to particulate material; bioavailability; bioaccumulation in invertebrates; and trophic transfer to predators. Important components of the methods included (1) empirically determined environmental partitioning factors between water and particulate material that quantify the effects of dissolved speciation and phase transformation; (2) concentrations of selenium in living and non-living particulates at the base of the foodweb that determine selenium bioavailability to invertebrates; and (3) selenium biodynamic foodweb transfer factors that quantify the physiological potential for bioaccumulation from particulate matter to consumer organisms and prey to their predators.

For this modeling effort, largemouth bass was used as the example fish. Although this is not a covered fish species, there are sufficient data to develop relationships between water and fish concentrations, and largemouth bass is a voracious consumer—a high level consumer relative to the covered fish species—and would show effects of bioaccumulation.

The source-water concentrations used in the model are listed in Table D-14. Modeling methods are described more fully in Attachment D.B.

## Table D-14. Historical Selenium Concentrations in the Five Delta Source Waters for the Period 1996–2010

Source Water	Sacramento River <sup>a</sup>	San Joaquin River <sup>b</sup>	San Francisco Bay <sup>a</sup>	East Side Tributaries <sup>c</sup>	Agriculture in the Delta <sup>a</sup>
Mean (μg/L) <sup>d</sup>	0.32	0.84	0.09	0.1	0.11
Minimum (μg/L)	0.04	0.40	0.03	0.1	0.11
Maximum (μg/L)	1.00	2.80	0.45	0.1	0.11
75th percentile (µg/L)	1.00	1.20	0.11	0.1	0.11
99th percentile (µg/L)	1.00	2.60	0.41	0.1	0.11
Data Source	USGS Website 2010	SWAMP Website 2009	SFEI Website 2010	None	Lucas and Stewart 2007
Station(s)	Sacramento River at Freeport	San Joaquin River at Vernalis (Airport Way)	Central-West; San Joaquín River near Mallard Is. (BG30)	None	Mildred Island, Center
Date Range	1996-2001, 2007-2010	1999-2007	2000-2008	None	2000, 2003– 2004
ND Replaced with RL	Yes	Yes	Yes	Not applicable	No
Data Omitted	None	Pending Data	None	Not applicable	No
No. of Data Points	62	453	11	None	1

Sources: U.S. Geological Survey Website 2010; SWAMP Website 2009; San Francisco Estuary Institute Website 2010; Lucas and Stewart 2007.

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#### D.5.2.2.2 Modeling Results—Selenium

Note to reviewers: these modeling results will be finalized in the EIR/EIS. The information below is preliminary and subject to update.

Selenium concentrations in the water column for the EBC2\_ELT/LLT, and for the preliminary proposal (PP\_ELT and PP\_LLT) are listed in Table D-15 and Table D-16. These tables also provide estimates for drought years only, when there is potential for greater effects. Generally, concentrations for both the early and late long-term were slightly lower for the preliminary proposal scenarios than the existing conditions. None of the resultant water concentrations of selenium exceeded 2  $\mu$ g/L, which is considered protective of fish species and is the lowest identified benchmark for selenium in water (see Table D-15 and Table D-16).

<sup>&</sup>lt;sup>a</sup> Dissolved selenium concentration.

<sup>&</sup>lt;sup>b</sup> Not specified whether total or dissolved selenium.

 $<sup>^</sup>c$  Dissolved selenium concentration in Mokelumne, Calaveras, and Cosumnes Rivers is assumed to be 0.1  $\mu g/L$  because of lack of available data and lack of sources that would be expected to result in concentrations greater than 0.1  $\mu g/L$ .

d Means are geometric means.

#### 1 Table D-15. Modeled Selenium Concentrations in Water for Early Long-Term

		Period Avera	ge Concentration	n (μg/L)
Location	Period*	EBC	EBC2_ELT	PP_ELT
Delta Interior				
Mokelumne River (SF) at Staten Island	All	0.260	0.261	0.247
	Drought	0.286	0.285	0.278
San Joaquin River at Buckley Cove	All	0.756	0.710	0.673
	Drought	0.721	0.649	0.595
Old River at Rancho del Rio	All	0.393	0.389	0.411
	Drought	0.315	0.313	0.304
Western Delta			72	
Sacramento River above Pt. Sacramento	All	0.312	0.311	0.312
	Drought	0.299	0.297	0.295
San Joaquin River at Antioch Ship Channel	All	0.312	0.310	0.324
	Drought	0.273	0.270	0.268
Sacramento River at Mallard Island	All	0.252	0.251	0.254
	Drought	0.213	0.210	0.209
	Drought	0.511	0.512	0.484

#### Notes:

 $\mu g/L = microgram(s)$  per liter.

Results compared to lowest of relevant thresholds—Level of Concern for the Grassland Bypass Project =  $2 \mu g/L$ . (Beckon et al. 2008.) Exceedances would be shaded and in italics—there are no exceedances.

These data are preliminary and are subject to change as BDCP analyses are finalized.

<sup>\*</sup> All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of dry and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).

#### 1 Table D-16. Modeled Selenium Concentrations in Water for Late Long-Term

		Period Avera	n (μg/L)	
Location	Period*	Existing Conditions	EBC2_LLT	PP_LLT
Delta Interior	•			
Mokelumne River (SF) at Staten Island	All	0.260	0.263	0.251
	Drought	0.286	0.287	0.279
San Joaquin River at Buckley Cove	All	0.756	0.693	0.700
	Drought	0.721	0.623	0.643
Old River at Rancho del Rio	All	0.393	0.388	0.411
	Drought	0.315	0.319	0.311
Western Delta	•			
Sacramento River above Pt. Sacramento	All	0.312	0.312	0.310
	Drought	0.299	0.297	0.295
San Joaquin River at Antioch Ship Channel	All	0.312	0.309	0.323
	Drought	0.273	0.272	0.270
Sacramento River at Mallard Island	All	0.252	0.251	0.250
	Drought	0.213	0.212	0.208
	Drought	0.511	0.531	0.499

#### Notes:

 $\mu g/L = microgram(s)$  per liter.

Results compared to lowest of relevant thresholds—Level of Concern for the Grassland Bypass Project =  $2 \mu g/L$ . (Beckon et al. 2008.) Exceedances would be shaded and in italics—there are no exceedances.

\* All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of dry and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).

These data are preliminary and are subject to change as BDCP analyses are finalized.

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Selenium concentrations in fish tissue fillets (largemouth bass) for both the EBC\_ELT/LLT and preliminary proposal (PP\_ELT and PP\_LLT) are listed in Table D-17 and Table D-18. These tables also provide estimates for drought years only, when there is potential for greater effects. Generally, concentrations for both the early and late long-term were slightly lower than the EBC. None of the fish tissue concentrations exceeded the Advisory Tissue Level (Office of Environmental Health Hazard Assessment 2008) of 2.5 mg/kg.

#### 1 Table D-17. Modeled Selenium Concentrations in Fish Fillets for Early Long-Term

		Period Average Co	oncentration (m	ng/kg, ww)
Location	Period*	Existing Conditions	EBC2_ELT	PP_ELT
Delta Interior				
Mokelumne River (SF) at Staten Island	All	0.35	0.35	0.32
	Drought	0.70	0.70	0.68
San Joaquin River at Buckley Cove	All	1.22	1.14	1.08
	Drought	1.95	1.74	1.59
Old River at Rancho del Rio	All	0.58	0.57	0.61
	Drought	0.79	0.78	0.75
Western Delta				
Sacramento River above Pt. Sacramento	All	0.44	0.44	0.44
	Drought	0.74	0.73	0.73
San Joaquin River at Antioch Ship Channel	All	0.44	0,43	0.46
	Drought	0,66	0.66	0.65
Sacramento River at Mallard Island	All	0.33	0.33	0.33
	Drought	0.49	0.49	0.48
	Drought	1.34	1.35	1.27

#### Notes:

mg/kg = milligram per kilogram; ww = wet weight.

Results compared to Advisory Tissue Level = 2.5 mg/kg. (Office of Environmental Health Hazard Assessment 2008.) Exceedances are shaded and in italics—there are no exceedances

\* All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of dry and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index).

These data are preliminary and are subject to change as BDCP analyses are finalized.

#### 1 Table D-18. Modeled Selenium Concentrations in Fish Fillets for Late Long-Term

		Period Average Co	oncentration (m	ng/kg, ww)
Location	Period*	Existing Conditions	EBC2_LLT	PP_LLT
Delta Interior				
Mokelumne River (SF) at Staten Island	All	0.35	0.35	0.33
	Drought	0.70	0.70	0.68
San Joaquin River at Buckley Cove	All	1.22	1.11	1.12
	Drought	1.95	1.67	1.72
Old River at Rancho del Rio	All	0.58	0.57	0.61
	Drought	0.79	0.80	0.77
Western Delta	•		72	
Sacramento River above Pt. Sacramento	All	0.44	0.44	0.43
	Drought	0.74	0.73	0.73
San Joaquin River at Antioch Ship	All	0.44	0,43	0.46
Channel	Drought	0.66	0.66	0.66
Sacramento River at Mallard Island	All	0.33	0.33	0.33
	Drought	0.49	0.49	0.48
	Drought	1.34	1.40	1.31

#### Notes:

mg/kg = milligram per kilogram; ww = wet weight.

Results compared to Advisory Tissue Level = 2.5 mg/kg. (Office of Environmental Health Hazard Assessment 2008.) Exceedances would be shaded and in italics—there are no exceedances

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The elevated concentrations in fish under drought conditions of 4.68 mg/kg (EBC2\_ELT) and 4.5 mg/kg (EBC2\_LLT) were estimated to decrease under the preliminary proposal. Estimated concentrations of selenium decreased in whole-body fish for EBC2 and PP for both early long-term (ELT) and late long-term (LLT) are listed in Table D-19 and Table D-20. Modeled selenium concentrations under all scenarios were below the level of concern for whole-body fish (lower-end range) (Beckon et al. 2008) of 4 mg/kg, except at the San Joaquin River at Buckley Cove location.

<sup>\*</sup> All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of dry and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index). These data are preliminary and are subject to change as BDCP analyses are finalized.

#### 1 Table D-19. Modeled Selenium Concentrations in Whole-Body Fish for Early Long-Term

		Period Average C	oncentration(n	ng/kg, dw)
Location	Period*	Existing Conditions	EBC2_ELT	PP_ELT
Delta Interior	•			
Mokelumne River (SF) at Staten Island	All	1.16	1.17	1.10
	Drought	2.06	2.06	2.00
San Joaquin River at Buckley Cove	All	3.38	3.18	3.01
	Drought	5.21	4.68	4.30
Old River at Rancho del Rio	All	1.76	1.74	1.84
	Drought	2.27	2.26	2.19
Western Delta			7/2	
Sacramento River above Pt. Sacramento	All	1.39	1.39	1.40
	Drought	2.16	2.14	2.13
San Joaquin River at Antioch Ship	All	1.39	1.39	1.45
Channel	Drought	1.97	1.95	1.93
Sacramento River at Mallard Island	All	1.13	1.12	1.14
	Drought	1.53	1.52	1.50
	Drought	3.68	3.70	3.49

#### Notes:

dw = dry weight; mg/kg = milligram per kilogram.

Results compared to Level of Concern for whole-body fish (lower end range) = 4 mg/kg. (Beckon et al. 2008.) Exceedances are shaded and in italics.

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<sup>\*</sup> All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of dry and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index). These data are preliminary and are subject to change as BDCP analyses are finalized.

#### 1 Table D-20. Modeled Selenium Concentrations in Whole-Body Fish for Late Long-Term

		Period Average C	oncentration(n	ng/kg, dw)
Location	Period*	Existing Conditions	EBC2_LLT	PP_LLT
Delta Interior	•			
Mokelumne River (SF) at Staten Island	All	1.16	1.18	1.12
	Drought	2.06	2.07	2.01
San Joaquin River at Buckley Cove	All	3.38	3.10	3.13
	Drought	5.21	4.50	4.64
Old River at Rancho del Rio	All	1.75	1.73	1.84
	Drought	2.28	2.30	2.24
Western Delta				
Sacramento River above Pt. Sacramento	All	1.39	1.39	1.39
	Drought	2.16	2.15	2.13
San Joaquin River at Antioch Ship	All	1.39	1.38	1.44
Channel	Drought	1.97	1.96	1.95
Sacramento River at Mallard Island	All	1.13	) 1.12	1.12
	Drought	1.53	1.53	1.50
	Drought	3.68	3.83	3.60

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dw = dry weight; mg/kg = milligram per kilogram.

Results compared to level of concern for whole-body fish (lower end range) = 4 mg/kg. (Beckon et al. 2008.) Exceedances are shaded and in italics.

#### **Uncertainty Analysis**

Modeling results are based on selenium water data for years 2010 and earlier. As previously discussed, selenium discharges from the Grassland watershed, a main contributor of selenium to the San Joaquin River and the Delta, must continue to decrease to meet relatively new criteria. The loading from the Grassland Project Area and resultant concentrations in the San Joaquin River are expected to continue to decline and will greatly diminish the source of selenium to the San Joaquin River and the Delta as a whole. The water and fish tissue modeling results does not account for this future decrease in selenium in the system and likely overestimates concentrations with the preliminary proposal water operations.

#### D.5.2.2.3 Changes in Proportion of San Joaquin Water in the Delta

Because the San Joaquin watershed historically has been a major source of selenium to the Delta, there is a concern that water operations, and specifically reduced flows in the Sacramento River, under the preliminary proposal could result in an increased proportion of San Joaquin water in the Delta, and with it increased selenium concentrations. DSM2 model results were used to track source water in the Delta. Results showing the difference in annual average contribution from the San

<sup>\*</sup> All: Water years 1975–1991 represent the 16-year period modeled using DSM2. Drought: Represents a 5-consecutive year (water years 1987–1991) drought period consisting of dry and critical water-year types (as defined by the Sacramento Valley 40-30-30 water year hydrologic classification index). These data are preliminary and are subject to change as BDCP analyses are finalized.

Joaquin River in the south Delta and Suisun Bay are presented in Table D-21. South Delta was chosen because of its proximity to the San Joaquin River. Suisun Bay was selected because elevated levels of selenium have been detected, mainly in biota, in the area. Also, Suisun Bay is near oil refineries where elevated selenium concentrations have been an issue.

Table D-21. Difference in Annual Average Proportion of San Joaquin River Contribution to Water Flow at South Delta and Suisun Bay

	South Delta—Change Contri	in San Joaquin River bution	Suisun Bay—Change in San Joaquin River Contribution		
	Percent Difference EBC2_ELT to PP_ELT	Percent Difference EBC2_LLT to PP_LLT	Percent Difference EBC2_ELT to PP_ELT	Percent Difference EBC2_LLT to PP_LLT	
1976	-1	-2	0	0	
1977	-4	-1	0	0	
1978	14	15	2	2	
1979	5	6	_1	1	
1980	6	7	1	1	
1981	-3	-4	0	0	
1982	17	21	4	3	
1983	22	19	9)	7	
1984	12	14	5	5	
1985	-2	-3	0	0	
1986	6	6	1	1	
1987	-7	-5	0	0	
1988	0	3	0	0	
1989	-1	8	0	0	
1990	-1	-1	0	0	
1991	-2	-7	0	0	
Average	4	5	4	1	

Results presented in Table D-21 show variation in the south Delta. The preliminary proposal actions would result in a less than 10% annual average increase in San Joaquin River water in the south Delta relative to other source waters (including the Sacramento River). For water years 1978, 1982, 1983, and 1984, the proportion of San Joaquin water is higher (12 to 22%). Preliminary proposal actions will have little to no effect on the proportion of San Joaquin water that flows to Suisun Marsh. Again, 1983 has the highest proportion of San Joaquin water present (9% for ELT and 7% for

#### D.5.2.3 Restoration

LLT).

In addition to preliminary proposal water operations effects described above, selenium concentrations in water and covered fish tissues may be affected by mobilization of selenium in restoration areas. Because the bioavailability of selenium increases in an aquatic system, inundation of ROAs could mobilize selenium sequestered in sediments and increase exposure of covered fish species. The rate at which selenium will become mobilized as part of restoration will depend on the amount of selenium stored in the sediments, the length of inundation, and whether sufficient time

allows the selenium to cycle through the aquatic system and into the food chain. It is likely that the highest concentrations of selenium will be mobilized during the initial flooding but will taper off with time; the length of time for the majority of selenium to flush out is not currently known and would need to be evaluated on a site-specific basis. Given that the San Joaquin River historically has delivered selenium to the Delta, the South Delta ROA has the most potential for mobilization of selenium.

In the long term, selenium inputs to the Delta should decrease as the proportion of agricultural lands decreases as a result of land use changes, including restoration to marsh habitat by the BDCP; selenium no longer would be concentrated by irrigation and leaching of these formerly farmed areas. This is especially true of the south Delta, where selenium in near-surface soils could be mobilized, but additional concentration from irrigation will cease. In contrast to the benefit of stopping application of pesticides to restored farmland, the benefit associated with selenium likely will be low, as selenium actually is leached out of the soils by agricultural use, not applied.

#### D.5.2.3.1 Selenium Summary

Quantitative modeling of selenium concentrations suggests that the preliminary proposal water operations would have from no effect to a positive effect on selenium in water and fish tissues. The only exceedances for fish tissues were for fish fillets and whole-body fish at Buckley Cove on the San Joaquin River during drought conditions. At Buckley Cove, benchmarks were exceeded for existing conditions (EBC2) and existing conditions early long-term (EBC2\_ELT); the early long-term concentrations were lower under the preliminary proposal (PP\_ELT). It is not surprising that the highest concentrations of selenium were estimated for the San Joaquin River, as this is the recognized primary source of selenium to the Delta. Future required reductions in selenium sources in the San Joaquin watershed should result in lower concentrations than those estimated by the model.

Source-water fingerprinting analysis indicates that preliminary proposed water operations will not result in a significant increased proportion of San Joaquin water at Suisun Bay. Proportions of San Joaquin water in the south Delta could increase by as much as 20%. Given the expected decrease in selenium contributions from the San Joaquin River and modeling results indicating that selenium concentrations will not exceed criteria in the south Delta, no effects on selenium concentrations as a result of preliminary proposal water operations are identified.

Selenium currently sequestered in soils could be mobilized and become more bioavailable as a result of inundation of restoration areas. The magnitude of this mobilization of selenium and resultant increases in concentrations in both water and covered species would need to be determined on a site-specific basis. The potential is highest for increased mobilization of selenium in and near the San Joaquin River and the South Delta ROAs, where selenium concentrations in soils are expected to be highest.

## D.5.3 Copper

## D.5.3.1 Copper—Location, Environmental Fate, and Transport

Copper (Cu) is a naturally occurring element that is present in water, air, and many soils in the environment. It is an essential trace element required by many plants and animals at low concentrations but can be toxic at elevated concentrations. In a non-aqueous environment, copper

1 tends to adhere to soils and is relatively immobile. In an aqueous system, copper is considered one 2 of the more mobile heavy metals. It partitions between sediment and particulates, and as 3 particulates, it is taken up by low trophic levels or complexes with organics or inorganics in the 4 water column. Typically it will occur in one of two oxidation states, cuprous ion (Cu<sup>1+</sup>) and cupric 5 ion (Cu<sup>2+</sup>) (U.S. Environmental Protection Agency 2009). Toxicity is much higher for the Cu<sup>2+</sup> ion, 6 than for the Cu<sup>1+</sup> ion and the copper that is organically complexed (Buck et al. 2007; Manahan and 7 Smith 1973; Sunda and Guillard 1976). 8 Although copper is not listed in the 303(d) list in the Delta, it is of concern mainly because of its 9 widespread use in pesticides. In the Delta, anthropogenic sources of copper include 10 pesticides/herbicides, mine drainage, brake pads, and anti-foulants (such as paint used on boat bottoms) (U.S. Environmental Protection Agency 2009). Because agriculture is the dominant land 11 12 use in the Delta, use of pesticides/herbicides is a dominant source of copper to the environment. 13 Mine drainage also has been a historical source of copper to the Delta. The Iron Mountain Mines 14 Superfund Site, a former mine that released acid mine drainage to the Sacramento River upstream of 15 Keswick Dam, has been a significant source of copper and other metal contamination. However, the 16 Superfund Site is undergoing remediation that has decreased discharge of copper into the rivers, 17 and a TMDL has been implemented (Central Valley Regional Water Quality Control Board 2002). Following remediation, copper inputs from this mine should continue to decrease. 18 19 The current AWOC-Fresh Water-Chronic for copper in fresh water is derived on a site-specific basis 20 requiring the input of 10 separate site-specific parameters to calculate the criteria—temperature, 21 pH, DOC, calcium, magnesium, sodium, potassium, sulfate, chloride, and alkalinity. Because these 22 parameters vary depending on location, it is not possible to calculate a general AWQC-Fresh Water-23 Chronic for copper. 24 Overall, levels of copper in the Delta ecosystem do not appear to be significantly elevated. Copper 25 concentrations in the Sacramento River have been reported to be consistently low, with some seasonal fluctuation (Connon 2010; Domagalski 2008). Based on collection of 549 water samples 26 27 collected during critically dry, normal and wet years from 15 Delta stations, metals concentrations 28 did not exceed AWQC and did not show toxicity (Central Valley Regional Water Quality Control 29 Board 1998). 30 Bruns (1998) conducted water sampling between 1993 and 1995, compared both dissolved and 31 total copper results against EPA AWQC and other criteria, and reported concentrations below 32 criteria from almost all locations, including the Sacramento River. Because the criteria are 33 dependent on sample-specific water quality measurements (including hardness), the criteria varied 34 between sampling episodes. Significantly higher copper levels (at least an order of magnitude higher than all other results) that exceeded criteria were reported for Prospect Slough at the head of the 35 36 Yolo Bypass. 37 In general, the copper data sets discussed above indicate low levels of copper (less than 2 μg/L) 38 throughout the Delta waterways and elevated concentrations in agricultural drainage sloughs, and

in tributaries at the head of the Yolo Bypass.

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#### 1 D.5.3.2 Copper—Effects of Preliminary Proposal Conservation Measures

#### 2 **D.5.3.2.1** Water Operations

- 3 Preliminary proposal water operations will result in decreased flow in the Sacramento River under
- 4 certain conditions. However, because copper concentrations are consistently low throughout the
- 5 Sacramento River (less than 2 μg/L) and copper concentrations in the Sacramento River watershed
- 6 have been tied to flow rates, appreciable impact on copper concentrations is not expected.

#### 7 D.5.3.2.2 Restoration

- 8 Restoration of agricultural lands under the preliminary proposal will have two outcomes relative to
- 9 copper: copper contained in soils may become more bioavailable, and copper in pesticides that
- would have been applied to the agricultural land will be subtracted from the total Delta copper
- 11 loads.
- 12 In general, the copper data sets discussed above indicate low levels of copper (less than 2 μg/L)
- throughout the Delta waterways, and elevated concentrations in agricultural drainage sloughs.
- Although data were not identified, it is assumed the agricultural soils will contain some level of
- copper given its affinity for soils in a terrestrial environment. A study of copper mobilization and
- 16 bioavailability following multiple floodings of copper-enriched agricultural soils in the Everglades
- 17 (Hoang et al. 2008) presents some relevant findings: (1) the amount of copper mobilized into the
- aguatic system depended on the concentrations in the soils, DOC, alkalinity, and soil characteristics;
- 19 (2) copper concentrations in soils did not change much after multiple (four) floodings; (3) total
- dissolved copper in the water column did not decrease after several flooding events; and (4) the
- 21 proportion of the more toxic cupric ion (Cu<sup>2+</sup>) increased with the number of flooding episodes and
- decreased DOC.
- These findings suggest that formerly agricultural ROAs, which are likely to have elevated levels of
- copper in soils, will result in some level of increased copper in the aquatic system over an
- 25 undetermined time period. Currently, information on the concentrations of copper in soils of specific
- ROAs is insufficient to estimate the increase in concentrations.
- 27 Restoration of agricultural land to marshes and floodplains will result in decreased application of
- copper-containing pesticides and decreased copper loading to the Delta. This net benefit at least
- 29 partially will counter the copper introduced to the aquatic system through mobilization during
- 30 inundation.

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## D.5.4 Ammonia/um

## 32 D.5.4.1 Ammonia/um—Location, Environmental Fate, and Transport

- Ammonia is present in water in two forms: as un-ionized ammonia (NH3+), also sometimes referred
- to as free ammonia, and as a positively charged ammonium ion (NH4+). These two forms are
- 35 collectively referred to as total ammonia or ammonia plus ammonium. Generally, environmental un-
- ionized ammonia is more toxic to fish, and ammonium is taken up by plants and algae as a nutrient
- and can drive algae blooms and growth of invasive species (Jabush 2011).
- The primary source of total ammonia in the Delta is effluent discharged from WWTPs, and the
- 39 primary contributing treatment facility is the Sacramento Regional WWTP (Jassby 2008). The

1 Sacramento plant is the source of the largest wastewater effluent discharge to the Delta (Jassby 2 2008), contributing an average of 141 million gallons per day (mgd) and accounting for 1 to 2% of 3 the river water volume (Foe et al. 2010). The facility is also the largest source of total ammonia 4 discharge to the Delta, making up 90% of the Sacramento River ammonia load (Jassby 2008). The 5 Stockton Regional Wastewater Control Facility historically had been an important source of the 6 ammonia load to the Delta via the San Joaquin River. This is no longer the case, as the Stockton 7 facility has upgraded its treatment systems in recent years to include technology to remove 8 ammonia and ammonium from effluent before discharge to the river (City of Stockton 2011). 9 For ammonia, there is a current EPA AWQC dated 1999, and an updated draft AWQC dated 2009 10 that has not yet been finalized (Table D-22). Both the current (1999) and draft (2009) AWQC for total ammonia as nitrogen are dependent on site-specific temperature and pH. The draft AWOC is 11 also dependent on the presence or absence of unionid mussels. AWQC for ammonia (total as N) for 12 13 both the current criteria and the draft criteria are listed in TableD-22. For ease of comparison, only

#### Table D-22. Ambient Water Quality Criteria for Ammonia

AWQC at a temperature of 25°C and pH of 8 are listed.

	Draft 2009 Ammonia Criteria (at pH 8 and 25°C)	Current 1999 Ammonia Criteria (at pH 8 and 25°C)
Acute	2.9 mg N/L mussels present	5.6 mg N/L salmon present
	5.0 mg N/L mussels absent	
Chronic	0.26 mg N/L mussels present	1.2 mg N/L fish early life stages present
	1.8 mg N/L mussels absent	
Source: <http: td="" w<=""><td>vater.epa.gov/scitech/swguidance/standards,</td><td>/criteria/aqlife/pollutants/ammonia/factsheet2.cfm&gt;.</td></http:>	vater.epa.gov/scitech/swguidance/standards,	/criteria/aqlife/pollutants/ammonia/factsheet2.cfm>.

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A recent study indicated that biota can be affected at concentrations as low as 0.38 mg/L of total ammonia nitrogen, based on a study of Delta copepods by Teh and coauthors (2011).

The current NPDES permit (2010) for the Sacramento WWTP contains both new and interim standards for ammonia. The current NPDES permit also prohibits discharge to the Sacramento River when there is less than a 14:1 (river:effluent) flow ratio over a rolling 1-hour period available in the Sacramento River. In addition, to comply with new standards (Table D-23), the Sacramento plant will need to install new systems to reduce ammonia concentrations in effluent. Compliance with new effluent limits will be required as of December 1, 2020, or once the new systems are in place, whichever occurs first (Central Valley Regional Water Quality Control Board 2010). However, this permit is being appealed and may not be upheld.

## Table D-23. Sacramento and Stockton Wastewater Treatment Facility Effluent—National Pollution Discharge Elimination System Permit Limits

	Units	Sacramento Effective 2010 (Interim) Average Daily	Sacramento Effective 2020 (New) Average Daily			
Ammonia, total as N	mg/L	33	1.8			
	lb	49,400	2,720			
Design flow mgd 181 181						
Source: Central Valley	Source: Central Valley Regional Water Quality Control Board 2010.					

The Sacramento Regional County Sanitation District (2011) reported the following ammonia concentrations in effluent from the Sacramento WWTP for the year 2010: average 24 mg/L (parts per million [ppm]); minimum 19 mg/L; and maximum 39 mg/L. Along with influent and effluent testing, the new 2010 NPDES permit requires that the Sacramento River (effluent-receiving water) be tested for ammonia, along with other parameters.

Ammonia concentrations in the Sacramento River were evaluated during a monitoring program conducted in 2009 and 2010. Water samples were collected on a monthly basis from 21 locations throughout the Delta, with a focus on tracking concentrations of ammonia downstream of the Sacramento WWTP (Foe et al. 2010). None of the ammonia data collected for 344 samples over 1 year exceeded the EPA chronic criterion for early life stages of fish present in the Delta (Foe et al. 2010). Results of this study indicated elevated ammonia levels immediately downstream of the Sacramento WWTP, with almost all the ammonia attenuated 20 miles downstream of the discharge, as follows:

- Ammonia concentrations were higher downstream (highest average 0.46 mg/L) of the Sacramento WWTP than upstream (average 0.04 mg/L).
- The highest ammonia concentrations were detected at Hood, 7 miles downstream of the WWTP.
- Downstream of Hood, total ammonia concentrations dropped continuously to an average of 0.08 mg/L at Threemile Slough, 20 miles downstream of the WWTP.

# D.5.4.2 Ammonia/um—Effects of Preliminary Proposal Conservation Measures

#### D.5.4.2.1 Water Operations

Given the possible link established between ammonia from WWTPs and the POD (Dugdale et al. 2007; Wilkerson et al. 2006; Glibert 2010; Glibert et al. 2011), decreased dilution capacity of the Sacramento River and potential resultant increases in ammonia concentrations are of concern. Recent data (Foe et al. 2010) indicate that concentrations of ammonia downstream of the WWTP outfall do not currently exceed EPA AWQC. These conditions are maintained with a current allowed ammonia concentration in WWTP effluent of 33 mg/L (and measured maximum concentration of 39 mg/L). By 2020, effluent must be below 1.8 mg/L ammonia, an 18-fold decrease in ammonia concentrations. It would take a similar decrease in Sacramento River flows to achieve the current conditions, and few to no effects are expected from preliminary proposal actions on ammonia/um. This conclusion is supported by the following quantitative analysis.

To evaluate resultant ammonia concentrations in the Sacramento River, the average reported concentration of ammonia in Sacramento WWTP effluent (24 mg/L) was used to calculate the Sacramento River flow required to meet AWQC. As shown in Table D-24, the minimum flow in the Sacramento River needed to dilute effluent and meet the current AWQC of 1.2 mg/L in the Sacramento River would be 5,794 cubic feet per second (cfs).

## Table D-24. Sacramento River Flow Required to Dilute Sacramento Wastewater Treatment Plant Effluent

Average Effluent Ammonia Concentration	24 mg/L
Design flow	181 mgd (7,930.087 l/sec)
Ammonia load	190,322.1 mg/sec
River—Threshold not to exceed	1.2 mg/L
River—Upstream concentration	0.04 mg/L
River—Threshold not to exceed	1.16 mg/L
Threshold flow to exceed (river)	164,070.8 l/sec (5,794 cfs)

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The DSM2 model output was analyzed to evaluate the percentage of time the minimum flow rate of 5,794 cfs would not be met. Results are presented in Table D-25 and Table D-26. Table D-25 presents the percentage of months the minimum flow would not be met for each scenario. Table D-26 shows the difference between EBC2\_ELT and LLT and the preliminary proposal (PP\_ELT and LLT) in the percent of time that Sacramento River flows at Freeport would fall below the required flow to dilute effluent. The effects of the preliminary proposal over the 82-year model run would be a 1.2% increase in the times that flows would be insufficient to meet AWQC for ammonia in August, and a 2.4% increase in October. In all other months, either no effects or a positive effect is indicated. The scenario is conservative, as concentrations in ammonia in Sacramento WWTP effluent are under order to decrease significantly.

In conclusion, changes in dilution capacity of the Sacramento River under the preliminary proposal would result from changes in upstream reservoir operations and are not expected to be significant.

Diversion of water to the Yolo Bypass is not expected to affect dilution capacity, as this will occur only during high river flows. The north Delta intake is downstream of Freeport and will not affect dilution of Sacramento WWTP discharges.

## Table D-25. Percentage of Months in CALSIM (82 Years) That Flows Are below Threshold (5,794 cfs) for Adequate Dilution of Sacramento WWTP Effluent to <1.2 mg/L Ammonia

	Percentage of Months with Inadequate Flows						
Month	EBC2	EBC2_ELT	EBC2_LLT	PP_ELT	PP_LLT		
January	0.0%	0.0%	0.0%	0.0%	0.0%		
February	0.0%	0.0%	0.0%	0.0%	0.0%		
March	0.0%	0.0%	0.0%	0.0%	0.0%		
April	0.0%	0.0%	0.0%	0.0%	0.0%		
May	1.2%	1.2%	2.4%	1.2%	2.4%		
June	0.0%	0.0%	0.0%	0.0%	0.0%		
July	0.0%	0.0%	0.0%	0.0%	0.0%		
August	0.0%	0.0%	0.0%	1.2%	0.0%		
September	0.0%	1.2%	2.4%	0.0%	0.0%		
October	0.0%	2.4%	0.0%	0.0%	2.4%		
November	0.0%	0.0%	2.4%	0.0%	1.2%		
December	0.0%	0.0%	0.0%	0.0%	0.0%		

## Table D-26. Percent Increase in the Number of Months That Flows Are below Threshold (5,794 cfs) for Adequate Dilution of Sacramento WWTP Effluent to <1.2 mg/L Ammonia

Month	EBC2_ELT-PP_ELT		EBC2_LLT-PP_LLT
January	0.0%		0.0%
February	0.0%		0.0%
March	0.0%		0.0%
April	0.0%		0.0%
May	0.0%		0.0%
June	0.0%		0.0%
July	0.0%		0.0%
August	-1.2%		0.0%
September	1.2%	ą	2.4%
October	2.4%		-2.4%
November	0.0%		1.2%
December	0.0%		0.0%

#### D.5.4.2.2 Restoration

Restoration conservation measures are not expected to significantly affect distribution or levels of ammonia/um in the Delta. Nitrogen is associated with fertilizers, which are used heavily throughout the Delta. However, WWTPs have been identified as the primary sources of ammonia, contributing 90% of the ammonia load to the Sacramento River. Thus, restoration of agricultural lands to marsh and floodplain is not expected to significantly affect ammonia concentrations.

Bay Delta Conservation Plan

Working Draft

D-45

January 2012

ICF 00610.10

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## D.5.5 Pyrethroids

### D.5.5.1 Pyrethroids—Location, Environmental Fate, and Transport

Pyrethroids are a group of synthetic chemicals currently used as insecticides in urban and agricultural areas. More than 1,000 synthetic pyrethroids have been developed (ASTDR 2003), but only 25 are registered for use in California (Spurlock and Lee 2008). Pyrethroids are powerful neurotoxins, have immunosuppressive effects, and can inhibit essential enzymes such as ATPases (Werner and Orem 2008). Pyrethroids can cause acute toxicity at concentrations as low as 1  $\mu$ g/L in fish (Werner and Orem 2008), and at lower levels between 2 and 5  $\mu$ g/L (0.002 and 0.005  $\mu$ g/L) in invertebrates. When various types of pyrethroid compounds are present together in an aqueous environment, the toxicity can be additive with increased toxic effects (Weston and Lydy 2010).

Overall pyrethroid use in the Delta has nearly quadrupled from 1990 to 2006 from approximately 27,000 kilograms per year (kg/yr) to more than 101,000 kg/yr in 2006 (U.S. Department of the Interior 2008) with five pyrethroids (lambda-cyhalothrin, permethrin, esfenvalerate, cypermethrin, and cyfluthrin) among the top agricultural insecticides in California (by acres treated) (Werner and Orem 2008). Pyrethroids are found in agricultural runoff, urban stormwater runoff, and in public WWTP effluent.

Significant sources of pyrethroids coming into the Delta from agricultural land include summer irrigation return flows from treated areas, winter stormwater runoff from orchards as a result of the common practice of applying pyrethroids during the winter season, and draining of excess surface water from rice fields during cultivation (Oros and Werner 2005). In addition to agricultural sources, recent studies have shown that WWTPs and urban runoff are important sources of pyrethroids to the Delta system (Weston and Lydy 2010). Pyrethroids have been detected at concentrations lethal to amphipods in urban runoff and effluent from the Stockton, Vacaville, and Sacramento WWTPs (Weston and Lydy 2010). However, receiving waters (San Joaquin River, American River, and Sacramento River) had fewer detections of pyrethroids at sublethal concentrations. Concentrations were higher in Vacaville creeks receiving effluent.

Pyrethroids have low water solubility; they do not readily volatilize and have a tendency to bond to particulates, settle out into the sediment, and not be transported far from the source. Once pyrethroids enter the Delta, they are easily adsorbed to suspended particles, organic material, soil, and sediments (Oros and Werner 2005). Because of the low-solubility nature of pyrethroids, it is estimated that 94% of pyrethroids used in the Central Valley remain at the application site and almost 6% degrade, with half life (the average time it takes for the concentration of the chemical to be reduced by one half) ranging from days to months, leaving only 0.11% ultimately available for transport through the Delta (Werner and Orem 2008). Seventy sediment samples were collected from agricultural drainage—dominated irrigation canals that run through 10 Central Valley counties. Analysis showed pyrethroids in 75% of the samples (Weston et al. 2004). However, pyrethroids were not often detected in agricultural drainage waters, demonstrating their strong affinity to sediments (Weston 2010).

Because pyrethroids have a very strong affinity for particulates, benthic organisms may be exposed to pyrethroids in sediment, and pelagic species could be exposed to pyrethroids adsorbed to particulates in the water column. Because pyrethroids are lipophilic, they have a tendency to bioaccumulatethrough the food chain (Werner and Orem 2008).

Breakdown of pyrethroids can occur through both chemical and biological processes and can take from days to months depending on a number of factors (Werner and Orem 2008). Half lives of pyrethroids are influenced by temperature and pH. At an alkaline pH, some pyrethroids can degrade through hydrolysis; however, most are stable at the relatively neutral pH of Delta waters (Werner and Oram 2008).

Many pyrethroids also are susceptible to degradation by sunlight, called photodegradation. The half life of different pyrethroids in water varies greatly with differences in their susceptibility to sunlight, from 0.67 day for cyfluthrin to 600 days for fenpropathrin (Werner and Oram 2008). High turbidity and the presence of plants can reduce ultraviolet-light penetration and increase pyrethroid half life, allowing increased residence times and the potential for greater adsorption to sediment.

# D.5.5.2 Pyrethroids—Effects of Preliminary Proposal Conservation Measures

#### D.5.5.2.1 Water Operations

As discussed above for ammonia, preliminary proposal water operations will result in reductions in Sacramento River flow at Freeport under certain conditions, mainly due to upstream reservoir operations. This reduction in flow could limit the dilution of Sacramento WWTP effluent and urban runoff, resulting in increased pyrethroid concentrations affecting covered fish species. In their study of pyrethroids in urban runoff, WWTPs, and receiving waters, Weston and Lydy (2010) reported few to no detections or toxicity to amphipods in Sacramento River water downstream of the Sacramento WWTP.

Weston and Lydy (2010) estimated loading from the Sacramento WWTP at 9g/day in the dry season and 13 g/day in the wet season. These estimates were based on median detected levels of total pyrethroids in effluent from three dry-weather (18.2 ng/L) and three wet-weather (14.2 ng/L) sampling events. Using a 13 g/day pyrethroid load and the lowest flow rate in the Sacramento River at Freeport in an 82-year period, estimated by the DSM2 at 5,110 cfs, the resultant concentration of pyrethroids in the Sacramento River is 7.19885 E-07 ng/L. This is consistent with Weston and Lydy's (2010) results that showed little to no detection of pyrethroids in the Sacramento River (Table D-27).

## Table D-27. Estimation of Resultant Pyrethroid Concentrations in Water under Preliminary Proposal Low-Flow Conditions in the Sacramento River

Pyrethroid Loading from Sacramento WWTP (Weston and Lydy 2010)	9 g/day		= 0.000104167 g/s	=0.104167 ng/s
Minimum Flow over 82 years with Preliminary Proposal	5,110 cfs		= 144,698.9497 L/sec	
Resultant Concentration	7.19885E-07	ng/L	Pyrethroids in the Sacr	amento River

Based on this analysis, the preliminary proposal water operations will have no effects on pyrethroids.

#### 1 D.5.5.2.2 Restoration

2 As discussed above, pyrethroids have been applied widely to agricultural land across the Delta; they

- 3 tend to stay sequestered in soils and therefore will be present in ROA soils. Pyrethroids have a
- 4 strong affinity for particulates, and would enter the water column as suspended particulates that
- 5 likely would settle out over time. The lack of pyrethroids in surface water samples where they are
- 6 present in sediments (Weston et al. 2004; Weston and State Water Resources Control Board 2010)
- 7 demonstrates the strong propensity for pyrethroids to remain in sediment. During inundation of
- 8 restoration areas, pyrethroids could be mobilized in the food chain via uptake by benthic organisms
- 9 or uptake of particulates by pelagic organisms.
- 10 Current information does not allow estimation of resultant pyrethroid mobilization due to
- preliminary proposal restoration. Concentrations of pyrethroids in ROA sediments and additional
- 12 research on mobilization and uptake into the food chain would be required. Given their affinity for
- soils, pyrethroids are not expected to spread far from the source area, and any suspension into the
- water column should be localized.

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## **D.5.6** Organochlorine Pesticides

## 16 D.5.6.1 Organochlorine Pesticides — Environmental Fate and Transport

- Organochlorine pesticides, specifically DDT, chlordane, and dieldrin, are legacy pesticides that are
- no longer in use but persist in the environment (Werner et al. 2008). These pesticides came into use
- from the late 1930s to the late 1940s and were phased out for general use in the 1970s; however,
- both chlordane and dieldrin remained in use until the late 1980s for termite control (Connor et al.
- 21 2007). These pesticides are widespread throughout the Sacramento and San Joaquin River
- watersheds and the Delta from widespread agricultural use (Conner et al. 2007).
- Organochlorine pesticides have a very low solubility in water and are very persistent in the
- 24 environment. DDT will degrade to dichlorodiphenyldichloroethane (DDD) and
- dichlorodiphenyldichloroethene (DDE), but these toxic by-products have very long half lives. The
- 26 Central Valley Water Board Agricultural Waiver Program recently reported detections of DDT and
- other organochlorine pesticides in Delta agricultural ditches and drainage channels (Werner et al.
- 28 2008). Because they do not dissolve in water, organochlorine pesticides enter the food chain in
- 29 particulate form, mainly through uptake by benthic fauna. They are strongly lipophilic and
- 30 biomagnify through the food chain, resulting in high concentrations in high trophic levels.
- 31 The current AWQC-Fresh Water-Chronic for the organochlorine pesticides of concern in the Delta—
- 32 DDT, chlordane, and dieldrin—are 0.001, 0.0043, and 0.056 µg/L, respectively. It should be noted,
- however, that the EPA anticipates future revisions to the criteria.
- 34 The highest concentrations in sediments and the greatest loading of organochlorine pesticides are
- 35 thought to come from the western tributaries of the San Joaquin River, and high concentrations have
- been reported in San Joaquin River sediments (Gilliom and Clifton 1990 cited in Domagalski 1998).
- However, total concentrations in the water column were low, consistent with the strong affinity of
- organochlorine pesticides for sediments. Domagalski (1998) reported low concentrations in the water column in the San Joaquin River basin, and noted that the organochlorine pesticides were
- water column in the San Joaquin River basin, and noted that the organochlorine pesticides were highest in tributary sediments and appeared to be mobilized by storms and rainfall. A study
- 41 involving collection and analysis of 70 sediment samples over 10 counties in the Central Valley
- showed that organochlorine pesticides continue to be present in sediments, and at high

concentrations, especially in agricultural drainage canals (Weston et al. 2004). This study found DDT in almost all samples collected, with a median concentration of 6.9 ng/g, and a maximum concentration of 408 ng/g in a drainage canal. DDE and other organochlorine pesticides also were detected at high levels in other drainage canal sediments.

# D.5.6.2 Organochlorine Pesticides—Effects of Preliminary Proposal Conservation Measures

#### D.5.6.2.1 Water Operations

Preliminary proposal water operations are not likely to result in mobilization of organochlorine pesticides. In the San Joaquin watershed, where concentrations are highest, these chemicals are found primarily in sediments in tributaries draining agricultural areas, and are present at low concentrations in the water column. Preliminary proposal water operations would not result in increased flows in the tributaries that would mobilize organochlorine pesticides in sediments. No changes in the load or concentrations of organochlorine pesticides transported into the Delta by the San Joaquin River are anticipated.

Upstream reservoir operations under the preliminary proposal will result in decreased flows in the Sacramento River, as discussed in previous sections. Because organochlorine pesticides adhere to soils, mobilization would have to be facilitated by erosion of contaminated soils. As significant increases in flow velocity are not expected under the preliminary proposal, organochlorine pesticides are not expected to be mobilized. Thus, no effects on organochlorine pesticide distribution are expected under the preliminary proposal water operations.

#### D.5.6.2.2 Restoration

Organochlorine pesticides likely will be sequestered in the formerly agricultural soils in ROAs. The highest concentrations will be in the ditches, creeks, and drains that received agricultural discharges. Because these chemicals tend to bind to particulates, concentrations are typically highest in sediment. Flooding of formerly agricultural land is expected to result in some level of accessibility to biota through uptake by benthic organisms. Significant increases in organochlorine pesticides are not expected in the water column because these chemicals strongly partition to sediments. Exposures to the foodweb will be through intake by benthic fauna and to a lesser extent, through particulates in the water column to pelagic organisms.

Also, concentrations in the water column should be relatively short-lived because these pesticides settle out of the water column in low-velocity flow. If eroded and transported from an ROA, it is likely that the pesticides would not be transported very far from the source area and would settle out and be deposited close to the ROA.

## D.5.7 Organophosphate Pesticides

### D.5.7.1 Organophosphate Pesticides—Environmental Fate and Transport

Organophosphate pesticides (organophosphates) are human-made chemicals that are used for pest control in both urban and agricultural environments. Sources of diazinon and chlorpyrifos in the Delta are predominantly agricultural as the sale of these compounds for most nonagricultural uses has been banned in recent years. In the Delta, diazinon is applied to crops during the dormant

season (December–February) and irrigation or growing season (March–November) fairly equally (52% and 48%, respectively), while the majority of chlorpyrifos (97%) is applied to Delta crops during irrigation season (McClure et al. 2006).

Diazinon and chlorpyrifos have slightly different chemical properties that affect the way they behave in aquatic environments. Diazinon is fairly soluble and mobile and will bind only weakly to soil and sediment. Chlorpyrifos is less soluble than diazinon and less mobile because of its tendency to bind much more strongly to soil and sediment. Consequently, diazinon enters the Delta dissolved in runoff, while chlorpyrifos enters the Delta adsorbed to soil particles (McClure et al. 2006). Unlike organochlorine pesticides, organophosphates do not tend to bioaccumulate, as they are readily metabolized by most organisms. For example, diazinon in fish will be approximately 96% removed in just 7 days (McClure et al. 2006).

Surface water data indicate that concentrations are high for both diazinon and chlorpyrifos in back sloughs and small upland drainages, and concentrations are lower in both the main channels and main inputs to the Delta. High concentrations of chlorpyrifos also are found in Delta island drains, but concentrations of diazinon remain low in the same drains (McClure et al. 2006). In the past, elevated concentrations of diazinon and chlorpyrifos have been detected in the Sacramento and San Joaquin Rivers and in the Delta during particularly wet springs and after winter storm events (McClure et al. 2006), suggesting that increased flow with accompanying increased suspended loads will result in increased mobilization of both diazinon and chlorpyrifos.

In the 2006 Staff Report for the amendments to the Basin Plan for diazinon and chlorpyrifos, updated water quality objectives developed by California Department of Fish and Game for diazinon and chlorpyrifos were compared to a broad sample set (McClure et al. 2006). Authors summarize surface water data for diazinon from 1991 to 2005, and chlorpyrifos from 1988 to 2005, from a number of previous sampling programs and studies and compared results to the updated water quality objectives of 160 and 25 ng/L for diazinon and chlorpyrifos, respectively. For context, the current AWQC-Fresh Water-Chronic for diazinon is 170 ng/L (0.17  $\mu$ g/L). There is no AWQC-Fresh Water-Chronic for chlorpyrifos.

Locations where diazinon exceeded 160 ng/L in more than 10% of samples included Mosher Slough, San Joaquin River near Stockton, Stockton Diverting Channel, and French Camp Slough. Likewise chlorpyrifos results showed more than 10% of samples collected at these locations exceeded 25 ng/L, including Ulatis Creek, Mosher Slough, Middle Roberts Island Drain, French Camp Slough, Paradise Cut, and Stockton Diverting Channel.

# D.5.7.2 Organophosphate Pesticides—Preliminary Proposal Conservation Measures

#### D.5.7.2.1 Water Operations

Diazinon and chlorpyrifos concentrations are highest in the back sloughs and agricultural drains that receive agricultural drainage. Preliminary proposal water operations are not likely to have much effect on transport of these chemicals from the back areas; transport of the pesticides from these areas would be determined mostly by rains that would flush out the areas. When flushed during wet seasons, the Sacramento River would maintain the capacity to dilute the influx. As discussed in Section D.5.4 (Ammonia/um), reduced flows would occur during dry periods in the

Sacramento River, when the back tributaries would not be flushing out. In general, preliminary proposal water operations are not expected to affect organophosphate concentrations in the Delta.

#### D.5.7.2.2 Restoration

Organophosphate pesticides are likely present in ROA soils that would be inundated under preliminary proposal conservation measures. Because the solubility, tendency to adhere to soils and particulates, and degradation rates for these compounds vary, it is difficult to estimate the extent to which inundation would cause the toxins to be mobilized and more bioavailable in the aquatic system. Also, because organophosphate pesticides are metabolized by fish and do not bioaccumulate, effects on covered species would be limited, depending on the life stage.

# D.5.7.3 Herbicides Associated with Conservation Measure 13 Nonnative Aquatic Vegetation Control

CM13 Nonnative Aquatic Vegetation Control would involve applying existing methods used by the California Department of Boating and Waterways' (DBW's) *Egeria densa* and Water Hyacinth Control Programs. Following is a brief summary of the types of herbicides used and the known toxic effects. (Table D-28.)

DBW uses five common herbicides—Weedar 64® (2,4-D), Rodeo® (glyphosate), R-11® (NP & NPE), Sonar® (fluridone), and Reward® (diquat). Riley and Finlayson (2004) depict the detected concentrations in the environment and the lethal concentration, 50% (LC50) values (mg/L) for larval delta smelt, fathead minnow, and Sacramento splittail.

Table D-28. Summary of Toxicity Testing for Invasive Species Herbicides

Herbicides and Surfactant	Highest Detected Concentration(mg/L)	Delta Smelt LC50 (mg/L)	Fathead Minnow LC50 (mg/L)	Sacramento Splittail LC50 (mg/L)
Weedar 64® (2,4-D)	0.260	149	216	446
Rodeo® (glyphosate)	0.037	270	1,154	1,132
R-11® (NP & NPE)	0.167	0.7	1.1	3.9
Sonar® (fluridone)	0.012	6.1	5.7	4.8
Reward® (diquat)	0.110	1.1	0.43	3.7
LC50 = lethal concentration	, 50%.			

magnitude higher than detected concentrations in the environment and would not be expected to cause lethal or sublethal effects in larval fish (Riley and Finlayson 2004). However, the LC50 values for Reward®, and R-11® are lower and approach the levels found in the environment, with the highest concentrations being above the LC50 values for both fathead minnow and splittail larvae (Riley and Finlayson 2004). However, these levels were reduced to background levels within 24 hours of application (Anderson 2003). R-11® is a surfactant used with both Rodeo® and Weedar 64®. R-11 was virtually undetected in the environment and can be controlled by careful application on plant surfaces only (Riley and Finlayson 2004). In conclusion, it is unlikely that acute toxicity would occur with the application of herbicides, with the possible exception of Reward®. Exposure

Rodeo®, Weedar 64®, and Sonar® 96-h LC50 values for the three fish species are several orders of

Bay Delta Conservation Plan

Working Draft

D-51

January 2012

ICF 00610.10

levels are less than acute toxic levels, and the chemicals have short lives in the environment. Sonar®

should be examined more closely because of its longer persistence in the environment and application procedures that require repeated treatments in the same area (Riley and Finlayson 2004).

### D.5.7.4 Endocrine Disruptors—Environmental Fate and Transport

EDCs can interfere with the hormonal system in fish at extremely low (ng/L) concentrations, resulting in negative effects on reproduction and development (Bennett et al. 2008; Riordan and Biales 2008; Lavado et al. 2009). Implications for Delta fish communities include changes in population distributions (e.g., changes in sex ratios that may affect population dynamics) that may be contributing to the POD (Brander and Cherr 2010).

Major sources of EDCs in the Central Valley are thought to be pyrethroid pesticides from urban runoff (Oros and Werner 2005; Weston and State Water Resources Control Board 2010), WWTPs (Routledge et al. 1998), and rangelands (Kolodziej and Sedlak 2007). EDCs also include steroid hormones (such as ethinylestradiol, 17 $\beta$ -estradiol, and estrone), plant constituents, plasticizers, and other industrial by-products. Pyrethroids have been documented to pass through secondary treatment systems at municipal WWTPs at concentrations that are toxic to aquatic life, and still may be present in detectable concentrations following tertiary treatment (Weston and State Water Resources Control Board 2010). Runoff from manure-treated fields and rangelands where livestock have direct access to surface waters can result in introduction of excreted endogenous steroid hormones, including estrogens, androgens, and progestins (Kolodziej and Sedlak 2007). Cultivated fields may contribute naturally occurring estrogenic compounds, such as mycotoxins, and some agricultural pesticides and wetting agents (non-ionic detergents) can be converted to estrogenic compounds in the environment or in the liver.

Estrogenic activity is a measurement of the effects of EDCs in the environment; however, this measure does not provide information on the causative substances. Documenting presence of multiple EDCs in surface waters does not necessarily indicate the constituent(s) responsible for adverse effects on fish populations. For example, Lavado with others (2010) conducted a survey of surface waters from 16 locations in California that were analyzed for EDCs using bioassays (which indicate levels of estradiol equivalents [EEQs]) and analysis for steroid hormones, detergent metabolites, agrichemicals, and other anthropogenic contaminants indicative of pharmaceuticals and personal care products. Samples from two of the 16 survey locations with estrogenic activity identified were subjected to bioassay-directed fractionation to try to identify the contaminants responsible for the estrogenic activity. Results were inconclusive.

# D.5.7.5 Endocrine Disruptors—Effects of Preliminary Proposal Conservation Measures

#### D.5.7.5.1 Water Operations

Endocrine disruptors are a diverse group of chemicals, and it is not possible to evaluate fully the potential effects on the distribution and bioavailability of these chemicals from preliminary proposal water operations.

#### D.5.7.5.2 Restoration

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2 Given current knowledge, there is potential for endocrine disruptors associated with pesticides to

be present in ROA soils and mobilized by inundation of ROAs. Because the chemical characteristics

- 4 of this group are diverse, the compounds may become mobilized and more bioavailable as
- 5 suspended particulates in the water column, or in the dissolved phase in the water column. The type
- 6 of endocrine disruptors and the possibility of mobilization would need to be evaluated on a site-
- 7 specific basis, taking into consideration the types of pesticides historically used on the property.

#### D.5.8 Other Urban Contaminants

- 9 Development accounts for only 8% of land area in the Delta, but urban sources, and specifically
- WWTPs, have been identified as important sources of some toxins (see discussion of pyrethroids
- and ammonia in previous sections).
- The primary Delta urban centers are located in both the Sacramento River watershed (cities of
- 13 Sacramento and West Sacramento) and the San Joaquin River watershed (city of Stockton). Lead,
- 14 PCBs, and hydrocarbons (typically oil and grease) are common urban contaminants that are
- 15 introduced to aquatic systems via nonpoint-source stormwater drainage, industrial discharges, and
- 16 municipal wastewater discharges. Lead, PCBs, and oil and grease all tend to adhere to soils, although
- some lighter components of oil and grease can become dissolved in water. Because they adhere to
- particulates, they tend to settle out close to the source and likely will be found at highest
- concentrations adjacent to the urban areas. PCBs are very persistent, adsorb to soil and organics,
- and bioaccumulate in the food chain. Lead also will adhere to particulates and organics but does not
- 21 bioaccumulate at the same rate as PCBs. Hydrocarbons will biodegrade over time in an aqueous
- 22 environment and do not tend to bioaccumulate; thus, they are not persistent.
- Lead and hydrocarbons have not been identified on the 303(d) list, and information on their
- presence and distribution in the Delta is very limited. Thus, they are not considered in this effects
- analysis. PCBs are listed on the 303(d) list and are discussed below.

#### D.5.8.1 Polychlorinated Biphenyls

- 27 PCBs were banned in the late 1970s, but because of their persistence in the environment, they are
- still found in mostly urban soils and sediments. High levels of PCBs in environmental media and fish
- 29 have been studied extensively in San Francisco Bay, which historically has received large amounts of
- 30 urban runoff and industrial discharge. Although the north Delta, the Natomas east main drain in
- 31 Sacramento, and the Stockton Deep Water Ship Channel are listed on the 303d list of impaired
- 32 waters for PCB contamination (State Water Resources Control Board 2010), few data are available
- concerning current concentrations or distribution of PCBs in the Delta.
- However, studies have not been conducted to evaluate the concentrations or distribution of PCBs in
- 35 the Delta environment. Fish studies in the Delta have indicated the presence of PCBs in the food
- 36 chain, but little work has been done in characterizing PCB concentrations in surface water and
- 37 sediment, and identifying the source of PCBs. Because PCBs biomagnify through the food chain, and
- many of the larger fish migrate through the San Francisco estuary, including the Delta, the location
- of the PCB source cannot be identified through fish tissue analysis.
- 40 A study of largemouth bass from the Sacramento River demonstrated significantly higher levels of
- 41 PCBs in eggs from the river compared to hatchery-raised fish (Ostrach et al. 2008). Elevated

1 concentrations of PCBs were reported in tissues of fish near Stockton (Lee et al. 2002; Davis et al. 2 2000). Studies by deVlaming (2008) and Davis with others (2000) reveal that PCB concentrations in 3 fish tissue samples from the north Delta and the Stockton Deep Water Ship Channel exceeded 4 thresholds for human health. deVlaming's 2005 fish tissue composite samples also found elevated 5 PCB concentrations in the Mokelumne and Tuolumne Rivers. However, deVlaming points out that, as 6 lipophilic legacy contaminants, PCBs are expected to be found in higher concentrations in older, 7 fattier fish, such as those that were sampled. The Sacramento sucker consistently had the highest 8 PCB concentrations in these studies but should not be considered an appropriate model for other 9 species because of its high lipid content (deVlaming 2008). 10 Overall, deVlaming found that the results from the 2005 tissue samples indicate that while high 11 concentrations of PCBs can be found in older, fattier fish in specific regions of the Delta (north Delta, Sacramento, and Stockton), Delta PCB concentrations are generally below Office of Environmental 12 13 Health Hazard Assessment (OEHHA) screening values. In addition, deVlaming suggests that his 2005 14 results indicate that the north Delta may be eligible for 303d de-listing. Similarly, the 2008 TMDL for 15 PCBs in San Francisco Bay states that PCBs in the Delta are expected to attenuate naturally, thus 16 eliminating the need for implementing action to reduce PCBs in Delta waters. Based on the 17 information presented here, PCBs are not expected to be affected by preliminary proposal actions.

# D.6 Effects of Changes in Toxins on Covered Fish Species

## D.6.1 Summary of Conclusions

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The preliminary proposal involves substantial restoration that would be implemented throughout the Delta over the 50-year implementation period as well as changes in water operations that could change how some toxins move through the Delta. As discussed in previous sections of this appendix, and further below, few to no effects on toxins in the Delta are expected from preliminary proposal water operations. Restoration of land with metals and pesticides in soils that could be mobilized into the aquatic system when inundated is expected to increase the bioavailability of some toxins to covered fish species. Given the current understanding of the complex processes involved in mobilizing these toxins, it cannot be modeled or estimated with any confidence. This appendix provides a full conceptual framework to understand the relevant processes. Site-specific analyses of restoration areas will be required to estimate the magnitude of the effects. Important to this picture is that taking lands out of agricultural use will result in an overall reduction of agriculture-related toxin loading, including pesticides, copper, and in some cases, concentrated selenium in irrigation drainage.

In general, the following conclusions can be drawn.

- Preliminary proposal water operations will have few to no effects on toxins in the Delta.
- Preliminary proposal restoration will increase bioavailability of certain toxins, especially methylmercury, but the overall effects on covered fish species are expected to be localized and of low magnitude.
  - Available data suggest that species exposure to toxins would be below sublethal and lethal levels.

The long-term benefits of restoration will reduce exposure to existing toxins in the environment and eliminate sources.

The following sections provide additional detail on the specific effects of toxic constituents on covered fish species.

## D.6.2 Conclusion of Effects of Toxins on Covered Fish Species

Effects on covered fish species will depend on the species/life stage present in the area of elevated toxins and the duration of exposure. Release of toxic constituents from sediments (e.g., in restored areas) is tied to inundation, and so highest concentrations will occur during seasonal high water and to a lesser extent for short time periods on a tidal cycle in marshes. A full description of fish occurrence over the species' life cycle is included in Appendix A and is integrated into the following sections where appropriate.

#### D.6.2.1 Mercury

Model results presented in Section D.5.1.2.1 indicate that preliminary proposal water operations will not adversely affect covered fish species. However, BDCP restoration efforts have the potential to increase the exposure of fish to methylmercury mobilized during inundation of restored tidal wetlands and floodplains, which are used for rearing by covered fish species. The areas expected to have the highest potential for methylmercury are the Yolo Bypass and, to a lesser extent, the Mokelumne-Cosumnes River. The amounts of methylmercury mobilized and resultant effects on covered fish species are not currently quantifiable. Slotton and others (2000: 43) noted:

Results to date suggest that wetlands restoration projects may result in localized mercury bioaccumulation at levels similar to, but not necessarily greater than, general levels within their surrounding Delta subregion. Nevertheless, high methylation potential, flooded wetland habitat may be the primary source of methyl mercury production in the overall system...Careful monitoring will be essential to assess the actual effects of new wetlands restoration projects.

Also, Slotton and others (2000) have noted that inland silversides from areas adjacent to flooded Delta tracts similar to proposed restoration sites did not exhibit elevated methylmercury.

The following discussion is based on the assumption that some level of methylmercury will be mobilized at BDCP ROAs. It also should be noted that a methylmercury mitigation conservation measure is part of the BDCP, and requires integration of design elements into restoration projects to decrease methylmercury production.

#### D.6.2.1.1 Eggs

The direct exposure of salmonid, sturgeon, and lamprey eggs to increased levels of methylmercury as a result of the preliminary proposal would not occur because salmonid, sturgeon, and lamprey eggs are not present anywhere that restoration is proposed. It is possible that maternal transfer could occur, i.e., prespawned eggs could be exposed to methylmercury from adult consumption of contaminated prey. Splittail, delta smelt, and longfin smelt all spawn in or near areas that would be restored under the preliminary proposal and therefore have the potential for increased exposure to methylmercury. For delta smelt and longfin smelt that spawn directly downstream of the Yolo Bypass or other ROAs in the west or north Delta, exposure of the eggs to aqueous mercury could range from 9 to 14 days (delta smelt) and up to 40 days (longfin smelt). Exposure of splittail eggs would be even less, with eggs hatching in 3–7 days. It is not known what level of mercury would be

assimilated and transferred to the larvae. Mercury exposure in eggs can lead to egg failure and developmental effects, but the levels of mercury that would have these results are not fully understood.

#### D.6.2.1.2 Larvae and Juveniles

Effects of increased methylmercury are expected to be minimal for fish rearing in the Delta. Henery and others (2010) compared methylmercury in Chinook salmon confined in the Yolo Bypass with those from the Sacramento River and found that the fish that reared in the Yolo Bypass accumulated 3.2% more methylmercury than fish held in the nearby Sacramento River. However, it should be noted that the mean methylmercury concentration for fish in the floodplain was 0.0567  $\mu g/g$  and only two of the 199 individuals sampled had greater than 0.20  $\mu g/g$  tissue methylmercury (a whole-body threshold of potential importance for sublethal effects on fish for growth, reproduction, development, and behavior) (Beckvar et al. 2005 as cited by Henery et al. 2010: 561). In addition, the 3.2% increase observed should be considered in the context of the life stage, i.e., the fish would subsequently be leaving the Plan Area and therefore no longer would be exposed to elevated concentrations of mercury, while also growing considerably larger in the ocean and therefore diluting accumulated mercury in their increasing body mass.

Henery also found that the body mass of free-ranging Chinook salmon that reared in the floodplain grew at a rate of 3.5% per day, compared to 2.8% per day for Chinook salmon that reared in the adjacent Sacramento River. Therefore, it appears that the increased exposure to methylmercury in rearing salmonids generally would not be high enough to elicit measurable sublethal effects. This growth dilution effect would be even more pronounced in adult fish that grow to three orders of magnitude larger over their life span, making the amount of methylmercury tissue accumulation as a juvenile insignificant (Henery et al. 2010).

Unlike salmonids, juvenile and subadult green and white sturgeon spend considerable time in the Delta. Laboratory studies have shown that high concentrations of methylmercury (25–50 ppm) in sturgeon diet are required to elicit any sort of adverse effect (Kaufman pers. comm.; Lee et al. 2011). Such elevated levels of methylmercury would not be experienced in the preliminary proposal restoration areas or the Yolo Bypass. Although juvenile sturgeon spend more time than any other covered fish species in the Plan Area, they also have the fastest growth rate of any species. Accumulation of methylmercury in the body tissue thus is mediated by growth dilution from the rapidly increasing muscle mass (Kaufman pers. comm.). Total body burden of methylmercury may increase, but tissue concentration of methylmercury would be expected to remain relatively constant (Kaufman pers. comm.) Juvenile sturgeon are primarily benthivores, feeding mostly on secondary productivity in the food chain (small crustaceans, clams, etc.) and therefore would not bioaccumulate mercury as fast as a top predator.

Larvae and juvenile splittail, delta smelt, and longfin smelt feed very low on the food chain and, similar to sturgeon juveniles described above, would bioaccumulate methylmercury at low levels. Additionally, juvenile longfin smelt occur primarily in San Pablo Bay and San Francisco Bay where no restoration or effects from water operations related to the preliminary proposal would occur. Similarly, juvenile delta smelt occur primarily in the west Delta and Suisun Bay, where elevated levels of methylmercury from restoration are not likely, and in Suisun Marsh, where the potential for elevated methylmercury is also low. However, juvenile smelt remaining in the north Delta area would experience exposure from food in the Yolo Bypass and Cache Slough regions.

#### D.6.2.1.3 Adults

Central Valley adult salmonids do not feed during their time in the Delta (Sasaki 1966) and potentially would be exposed to the elevated methylmercury produced in this portion of the Delta through absorption from water through their gills. Additionally, they tend to stay in the main channels through the Delta, rather than the shallow, slow-moving waters of wetlands and floodplains. As a result of their limited time in the estuary and the tendency to migrate in the main channels, adult salmonids are not likely to be exposed to a significantly different quantity of methylmercury under the preliminary proposal than under current conditions. Elevated mercury levels in the East Delta subregion could be encountered at the confluence of the Mokelumne and Cosumnes Rivers, although the number of spawning occurrences in this area by covered fish species is relatively small.

Adult sturgeon would be using the preliminary proposal regions primarily as a pathway for spawning migration, although they do forage in the lowest preliminary proposal regions. Adult sturgeon would not accumulate high tissue loads of methylmercuryfor the same reason as the juveniles, coupled with the fact that they spend little time in areas that are projected to have increased methylmercury production. Analyses of white sturgeon from San Francisco Bay (albeit downstream of the Plan Area) found median mercury concentration in muscle below the screening level for human consumption concern of  $0.3~\mu g/g$  wet weight (Greenfield et al. 2000).

Although adult life stages of splittail, delta smelt, and longfin smelt feed and spawn in areas with potential for elevated methylmercury levels, they feed primarily on lower trophic level food sources and therefore do not accumulate methylmercury at rates as high as if they preyed on fish. Additionally, they are not expected to spend excessive amounts of time in these areas, so the uptake through their gills and food is expected to be minimal. Nevertheless, delta smelt have been shown to accumulate appreciable quantities of mercury: Bennett and coauthors (2001) found average levels of 0.18  $\mu$ g/g, which is just under the 0.20  $\mu$ g/g general threshold for effects on fish suggested by Beckvar and coauthors (2005 as cited by Henery et al. 2010: 561). There is no evidence for acute toxicity of mercury being related to recent declines of pelagic fish such as delta smelt and longfin smelt, although mercury, selenium, and copper may have had a chronic effect on these species (Brooks et al. 2011).

#### D.6.2.2 Selenium

As discussed in Section D.5.2, elevated selenium is recognized as a threat to fish in the Delta. However, few to no effects on selenium from preliminary proposal actions have been identified. Historically, the San Joaquin River has been a major source of selenium to the Delta; however, the selenium source is being addressed and selenium concentrations are decreasing. Further, modeling results indicate that preliminary proposal water operations would have few to no effects on selenium concentrations in water or fish tissue. Suisun Marsh has high levels of selenium in filter-feeding clams that bioaccumulate selenium and form the base of the food chain, which results in biomagnification to covered fish species. However, no mechanisms for the preliminary proposal actions to increase selenium in Suisun Marsh have been identified.

As a conservative approach, the following discussion of the possible effects of preliminary proposal actions on selenium in covered fish species assumes that some increase in selenium will occur under the preliminary proposal actions. Any increases are expected to be localized and associated with

inundation of ROAs, mainly in the south Delta, which receives input from the San Joaquin River, a historical source of selenium.

The bioaccumulation and effects of selenium on fish have much to do with their feeding behavior. The overbite clam, *C. amurensis*, accumulates selenium and is key to mobilizing it into the food chain. It is abundant in Suisun Bay, but the preliminary proposal is not expected to increase the contribution of selenium to this area given the distance from the San Joaquin River source (modeling results corroborate). Smelt, steelhead, and Chinook salmon would be expected to have low exposure to selenium as they are feeding on pelagic organisms that are able to excrete selenium at more than 10 times the rate of the benthic clam, *C. amurensis*. This is in contrast to sturgeon and splittail that are at risk for teratogenesis because of their diet preference for *C. amurenis*, and high concentrations of selenium bioaccumulated in their tissues, especially reproductive organs, liver, and kidneys. Deformities occur in developing embryos when selenium replaces sulfur in sulfur-rich hard tissues (Diplock 1976). For example, recent field surveys identified Sacramento splittail from Suisun Bay (where selenium concentrations are highest) that have deformities typical of selenium exposure (Stewart 2004). Both green and white sturgeon feed on C. amurensis in the three lower subregions (Suisun Bay, Suisun Marsh, and West Delta) but are not likely to be affected by the preliminary proposal-related changes in selenium because of the distance from the source area (Grassland in San Joaquin River basin). Modeling results corroborate this conclusion. Little is known about lampreys, but based on lamprey ammocoete occurrence in the Delta (mostly in the Sacramento River area), it is expected that their exposure to selenium-laden sediments and water would be minimal.

#### D.6.2.3 Copper

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Copper will be present in agricultural soils and could be mobilized by inundation of the ROAs, as it is fairly immobile in soils, but is very mobile in an aquatic system. Preliminary proposal water operations are not expected to have much effect on copper concentrations, although there is a slight chance of mobilization of copper from increased flow at the weir at the upstream end of the Yolo Bypass, where copper concentrations may be elevated.

Mobilized copper could have a temporary adverse effect on juvenile fish, namely salmonids, splittail, and smelt that rear in the Yolo Bypass. Additionally, splittail adults, eggs, and larvae may be exposed while in the bypass. Likewise, rearing juvenile and adult salmonids and sturgeon may be exposed in other ROAs previously used for agriculture.

It is difficult to establish precise concentrations at which copper is acutely toxic to fish, as a large number of water chemistry parameters (including temperature, pH, DOC, and ions) can affect the bioavailability of copper to the fish population (U.S. Environmental Protection Agency 2007). As discussed in Section D.5.3, copper is present in the Sacramento River at low concentrations (2  $\mu g/L$ ). Connon with others (2010) demonstrated that the median lethal concentration of dissolved copper at which 10% of delta smelt juveniles died after 7 days of exposure under experimental conditions (LC10) was 9.0  $\mu g/L$ ; 50% of juveniles died (LC50) when exposed to a median concentration of 17.8  $\mu g/L$ . Although 96-hour larval delta smelt mortality suggested higher concentrations than juveniles (median LC10 = 9.3  $\mu g/L$ ; median LC50 = 80.4  $\mu g/L$ ), these results were complicated by differences in exposure duration and experimental conditions (particularly for factors such as temperature and conductivity that may affect copper toxicity) (Connon et al. 2010).

Carreau and Pyle (2005) demonstrated that copper exposure during embryonic development of fathead minnows could result in permanent impairment of chemosensory functions but that the same exposure caused only temporary impairment in adults once copper is removed, suggesting that the specific life stage at the time of exposure also plays a role in the toxicity of copper to fish. Baldwin and coauthors (2003) reported inhibition of olfactory physiology in salmonids at concentrations of 6  $\mu$ g/L (background plus spiked concentration), indicating that low levels of copper over a short period of exposure could affect migratory ability in salmonids. Sandahl (2007) reported impairment of sensory functions and avoidance behavior in juvenile coho at copper concentrations of  $2\mu$ g/L. There is some evidence that larval delta smelt swimming velocity decreases as dissolved copper concentration increases, although experimental testing did not find statistical differences between test subjects and controls (Connon et al. 2010). Various delta smelt genes have been to shown to have altered expression in copper-exposed larvae (Connon et al. 2010).

Localized, short-term increases in copper concentrations are possible near ROA areas, but the length of time and the concentrations cannot be determined with available data. Overall, because copper concentrations are generally low in Delta waters, preliminary proposal actions are not expected to result in increased effects of copper on covered fish species. In fact, halting agricultural use and application of pesticides on restoration areas will result in decreased loading of copper to the Delta system and will provide a long-term net benefit to the ecosystem.

#### D.6.2.4 Ammonia

Based on the analysis presented in Section D.5.4, preliminary proposal actions are not expected to result in substantial increases in ammonia concentrations in the aquatic system that could affect covered fish species. Analysis of the ability of the Sacramento River to dilute ammonia discharges from the Sacramento WWTP indicates that resultant concentrations would be within ecologically acceptable limits under the preliminary proposal. Further, no addition or mobilization of ammonia to the aquatic system would result from restoration activities.

# D.6.2.5 Pyrethroids, Organophosphate Pesticides, and Organochlorine Pesticides

Based on the analyses in Sections D.5.5, D.5.6, and D.5.7, changes in concentrations of pyrethroids, organophosphate pesticides, and organochlorine pesticides resulting from the preliminary proposal are expected in the vicinity of agricultural land restored to marshes and floodplains. These chemicals either have a strong affinity for sediment and will settle out of the water column, or readily degrade in an aquatic system. Thus, it is expected that increases in concentrations due to preliminary proposal actions will be of relatively short duration and localized near ROAs. Specific areas of these elevated toxins have not been identified, but they can be expected in any of the ROAs. Preliminary proposal restoration will take these agricultural areas out of production, therefore eliminating the source and reducing these chemicals in the Delta system, providing a long-term ecological benefit.

Pyrethroids have been shown to be lethal as low as 1  $\mu$ g/L, although there are many different chemicals in this group with varying toxicities for fish. Likewise, little is known on the effects of organophosphates on fish, but elevated concentrations of organophosphates are more likely to affect the lower trophic levels that the covered fish species prey on than the fish directly (Turner 2002). As these pesticides are neurotoxins, behavioral effects are of primary concern; however, Scholz (2000) points out that the effects are not well understood. Scholz (2000) found that diazinon

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concentrations as low as 1 µg/L resulted in significant impairment of predator-alarm responses, and slightly higher concentrations of 10 µg/L caused the impairment of homing behavior in Chinook salmon. Organochlorine pesticides are neurotoxic, are likely carcinogenic, and have been implicated as endocrine disruptors because of their estrogenic nature and effects on reproductive development (Leatherbarrow et al. 2006). These pesticides are highly persistent and lipophilic, and as such, they strongly bioaccumulate (Werner et al. 2008). Because of their persistence in the environment and biomagnifications through the foodweb, the main concern with organochlorines is bioaccumulation in the higher trophic levels and implications for human consumption. However, organochlorine pesticides and degradation products can directly affect fish through toxicity to lower-level invertebrates on the food chain, and toxicity to small and early life stage fish, but there is little information specific to effects on individual species. Sublethal effects may include reproductive failure and behavioral changes. Ostrach's (2009) report suggests that largemouth bass have been experiencing reproductive failure due to organochlorine compounds in San Francisco Bay, which is likely due to concentrations accumulated through biomagnifications. Because they tend to adhere to soils and particulates, organochlorine compounds may take longer to flush out than some of the more environmentally mobile constituents discussed above (e.g., copper).

In the Delta, fish in higher trophic levels are particularly vulnerable to these pesticides, as the chemicals will biomagnify and bioaccumulate in their tissues. These fish include white and green sturgeon, salmonids, and lampreys. As smaller fish at lower trophic levels, smelt and splittail can be expected to have less biomagnification of these pesticides.

More detailed analysis of pyrethroid, organophosphate pesticide, and organochlorine pesticide effects would require site-specific information, but overall the preliminary proposal is not expected to substantially increase the potential exposure of fish because elevated bioavailability likely would be localized near ROAs and over a relatively short time period. Additionally, restoration of agricultural land will result in an overall reduction in these chemicals in the Delta system, with an overall net ecological benefit.

### D.6.3 Uncertainties and Information Needs

As discussed throughout this appendix, the amount of toxins that will be mobilized and made more bioavailable to covered fish species due to inundation of ROAs is uncertain. This uncertainty is most critical for methylmercury, and to a lesser extent for pesticides and other metals. For each of the toxins, the chemical-specific and site-specific factors that will determine resultant effects vary. Conservation CM12 is included in the BDCP to support site specific evaluation and monitoring of methylmercury production in restored areas. Data from this monitoring will assist in evaluating the effects of restoration actions and reduce the uncertainty associated with the potential exposure of covered fish to methylmercury mobilized by these actions.

## D.7 References

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#### **Personal Communications** D.7.2

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E ects of BDCP Actions on Water Quality



Uptake into foodchain

Via lower trophic levels and direct absorption by sh

### Transformation to Methylmercury

Increased solubility and toxicity



Restoration of Tidal Marsh and Floodplains

Methylation of mercury under intermittent ooding conditions

#### Mercury-containing Sediment

Source: Mercury from upstream mining operations has been transported by rivers

and deposited throughout the Delta

Highest Concentrations: Yolo Bypass/Cache Creek; Cosumnes/Mokelumne Con uence

# Bioaccumulation Model Development for Mercury Concentrations in Fish

#### 4.A.1 Introduction

Areas of enhanced bioavailability and toxicity of mercury (created through the mercury methylation process) exist in the Sacramento–San Joaquin River Delta (Delta), and elevated mercury concentrations in fish tissue produce estimates of exposure and risk to humans and wildlife. Consequently, the beneficial uses most directly affected by mercury are shellfish harvesting and commercial and sport fishing activities that pose a human health concern, and wildlife habitat and rare, threatened, and endangered species resources that can be exposed to bioaccumulation of mercury. Because of these concerns, mercury was the first total maximum daily load (TMDL) approved for San Francisco Bay in 2007 (San Francisco Bay Regional Water Quality Control Board 2006), and a methylmercury TMDL is in progress for the Delta (Central Valley Regional Water Quality Control Board 2008). The Delta and Suisun Marsh both are listed as impaired water bodies on the Clean Water Act Section 303(d) lists for mercury in fish tissue (State Water Resources Control Board 2007).

The conceptual model of mercury transport, fate, and risk for the Delta as used in this study shows important linkages among waterborne loading, waterborne concentrations, and water, sediment, and biotic processing of mercury and methylmercury. Mercury is strongly particle associated and tends to settle and accumulate in sediment deposition areas that facilitate mercury methylation by sulfur-reducing bacteria. From that point in the cycle, diet (rather than waterborne concentration) is the primary route for methylmercury exposure to fish, wildlife, and humans.

Mercury in largemouth bass was chosen as the representative measure of fish bioaccumulation for this study because bass tissue concentrations have been described recently over a wide area of the Delta. Consequently, the fish tissue concentrations of mercury could be linked in time and space with estimated waterborne concentrations of mercury and methylmercury to examine possible causal linkages. In addition, the California Regional Water Quality Control Board, Central Valley Region (Central Valley Water Board) already successfully used this general approach to link waterborne and largemouth bass mercury concentrations for broad areas of the Deta. However, for the preliminary proposal, it was desirable to examine fish tissue–water mercury linkages at defined locations rather than general Delta conditions over broad areas.

# 4.A.2 Mercury Concentrations in Water and Fish

The DSM2 output locations where whole-body largemouth bass data for mercury were available are shown on Table D.A-1 (tables are at the end of this attachment). The geometric mean mercury and methylmercury concentrations in water were estimated for selected DSM2 output locations and then used to estimate mercury concentrations in fish tissue (fillets).

The quarterly and annual average waterborne mercury and methylmercury concentrations for the DSM2 output locations are shown in Table D.A-1 (for Year 2000). Note that the first quarter DSM2

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- model results were discarded because the model "ramps up" for a new year, and the average values from those first months were distinctly lower than for the other quarters. Therefore, the annual average for the year was computed from the last three quarters.
- 4 Largemouth bass were chosen for modeling because they are popular sport fish, top predators, live 5 for several years, and tend to stay in the same area (that is, they exhibit high site-fidelity). 6 Consequently, they are excellent indicators of long-term average mercury exposure, risk, and spatial 7 pattern for both ecological and human health. Fish tissue concentrations were available from 1999 8 and 2000 at modeled locations; DSM2 estimated waterborne concentrations from those locations 9 were modeled on the year 2000 hydrology. The Sacramento River inflows and Cosumnes River were 10 the areas of highest fish tissue bioaccumulationof mercury. Bass had uniformly lower tissue 11 concentrations in the central Delta. The Central Valley Water Board TMDL tissue concentration goal
- for normalized 350-mm total length largemouth bass tissue is 0.24 mg/kg wet weight (ww) mercury
- for the Delta (Central Valley Regional Water Quality Control Board 2008).

# 4.A.3 Bioaccumulation Model Predicting Mercury in Fish

The largemouth bass tissue mercury concentrations were presented as edible fillet concentrations for fish normalized to 350 mm in total length as supplied directly by San Francisco Estuary Institute (SFEI) (2010). It is important to standardize concentrations to the same size fish at each location because of the well-established positive relationship between fish size and age and tissue mercury concentrations (Alpers et al. 2008).

Co-located fish fillet mercury concentrations were graphed against their corresponding values of waterborne mercury or methylmercury in standard, linear regression analyses using annual average and quarterly water values calculated using the SAS Institute's Statview 5 analytic software (SAS Institute 1998). The data were log-transformed to improve normality. The positive relationships with mercury were not as strong as with methylmercury. The best choice for a predictive model was the linear regression showing a statistically significant relationship between annual average waterborne methylmercury concentrations in water from the third quarter of the year and largemouth bass tissue mercury concentrations

Fish mercury (mg/kg ww) =  $10^{(4.217 + (Log methylmercury in water, \mu g/L \times 1.164))}$  [Eq.1]

The results of this regression model in can be compared to those using the alternative from the Central Valley Water Board TMDL model, which also predicts 350-mm normalized largemouth bass fillets from methylmercury in water. This comparison is shown in Table D.A-2. The Central Valley Water Board developed a model based on largemouth bass as grouped in major areas of the Delta compared to average methylmercury concentrations in water for those areas Central Valley Regional Water Quality Control Board 2008):

Fish mercury  $(mg/kg ww) = 20.365 \times ((methylmercuryin water, ng/L)^1.6374)$  [Eq. 2]

For the DSM2-estimated water concentrations for 2000, the Central Valley Water Board model consistently overpredicted the fish concentrations as compared to the regression model (mean of 0.719 mg/kg compared to 0.411 mg/kg) relative to the measured value of 0.446 mg/kg (Table D.A-2). For this reason, the regression model was used to predict bass fillet concentrations for this study. The Central Valley Water Board TMDL model was not established to predict fish tissue

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concentrations but to provide the linkage between the 0.24 mg/kg tissue mercury TMDL target and the waterborne goal of 0.066 ng methylmercury/L.

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#### Table D.A-1. Mercury and Methylmercury Concentration Estimates in Water at Selected Locations in the Delta

	Concentration (μg/L)							
	Second Quarter*		Third Quarter		Fourth Quarter		Annual Average	
DSM2 Output Location	Hg	МеНд	Hg	МеНд	Hg	MeHg	Hg	MeHg
Sacramento River RM 44	0.00410	0.00010	0.00410	0.00010	0.00410	0.00010	0.00410	0.00010
Mokelumne River downstream of Cosumnes	0.00856	0.00022	0.00845	0.00022	0.00855	0.00022	0.00852	0.00022
Cosumnes River	0.00860	0.00022	0.00860	0.00022	0.00860	0.00022	0.00860	0.00022
Cache Slough	0.00411	0.00010	0.00413	0.00010	0.00412	0.00010	0.00412	0.00010
Sacramento River at Isleton	0.00410	0.00010	0.00411	0.00010	0.00411	0.00010	0.00411	0.00010
San Joaquin River Potato Slough	0.00532	0.00013	0.00420	0.00010	0.00424	0.00010	0.00459	0.00011
Sherman Island	0.00479	0.00011	0.00450	0.00010	0.00475	0.00009	0.00468	0.00010
White Slough downstream of Disappointment Slough	0.00686	0.00016	0.00466	0.00012	0.00490	0.00013	0.00547	0.00014
Franks Tract	0.00546	0.00013	0.00426	0.00011	0.00429	0.00010	0.00467	0.00011
Big Break	0.00493	0.00012	0.00436	0.00010	0.00448	0.00010	0.00459	0.00011
Mildred Island	0.00699	0.00015	0.00461	0.00012	0.00509	0.00012	0.00556	0.00013
San Joaquin River Naval Station	0.00762	0.00016	0.00763	0.00016	0.00761	0.00015	0.00762	0.00016
	SW.			AND THE PARTY OF T	SERA.			

Notes:

\*First quarter DSM2 modeled water concentrations were not used because of model "ramp up" artifacts.

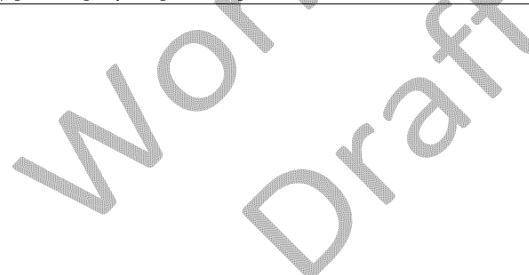
 ${\sf MeHg = methylmercury}\,.$ 

Hg = mercury.

RM = river mile.

#### Table D.A-2. Modeled and Measured Bass Fillet Mercury Concentrations

	Bass Tissue Concentration (mg/kg ww)			
Site	Measured Fish	Regression Model	Central Valley Water Board TMDL Model	
Sacramento River RM 44	0.869	0.364	0.470	
Mokelumne River downstream of Cosumnes	1.091	0.930	1.758	
Cosumnes River	0.895	0.926	1.745	
Cache Slough	0.559	0.372	0.484	
Sacramento River at Isleton	0.628	0.366	0.473	
San Joaquin River Potato Slough	0.365	0.413	0.560	
Sherman Island	0.323	0.371	0.482	
White Slough downstream of Disappointment Slough	0.226	0.525	0.785	
Franks Tract	0.265	0.420	0.574	
Big Break	0.226	0.390	0.518	
Mildred Island	0.226	0,498	0.729	
San Joaquin River Naval Station	0.352	0.621	0.996	
San Joaquin River Vernalis	0.739	0.583	0.912	
Geometric mean	0.446	0.493	0.719	
Maximum	1.091	0.930	1.758	
Minimum	0.226	0.364	0.470	
mg/kg ww = milligram per kilogram wet weight.				



# **Selenium Modeling Methods**

3	4.B.1	Bioaccumulation Model Development for
4		Selenium Concentrations in Whole-Body Fish,
5		Bird Eggs, and Fish Fillets

- Plan-related changes in waterborne concentrations of selenium in the Sacramento–San Joaquin
  River Delta (Delta) may result in increased selenium bioaccumulation and/or toxicity to aquatic and
  semi-aquatic receptors using the Delta. Historical fish tissue data and measured (at Vernalis) or
  DSM2-modeled (other locations) waterborne selenium concentrations for selected locations in
  2000, 2005, and 2007 were used to model water-to-tissue relationships, generally following
  procedures described by Presser and Luoma (2010).
- The output from the DSM2 model (expressed as percent inflow from different sources) was used in combination with the available measured waterborne selenium concentrations to model concentrations of selenium at locations throughout the Delta. These modeled waterborne selenium concentrations were used in the relationship model to estimate bioaccumulation of selenium in whole-body fish and bird eggs. Selenium concentrations in fish fillets then were estimated from those in whole-body fish.
- The data and processes used to develop the final models to estimate this selenium bioaccumulation are described in the following sections.

## 4.B.2 Selenium Concentrations in Water

- Dissolved selenium data were available for six inflow locations to the Delta. Whole-body largemouth bass data for selenium were available from the following DSM2 output locations.
- 23 Big Break

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- 24 Cache Slough at Ryer Island

- 28 Old River Near Paradise Cut
- 29 Sacramento River Mile (RM) 44
- 30 San Joaquin River Potato Slough

The geometric mean selenium concentrations from the inflow locations were combined with the modeled quarterly average percent inflow for each DSM2 output location to estimate waterborne selenium concentrations at selected DSM2 output locations.

The quarterly average mix of water from the six inflow sources was calculated from daily percent inflows provided by the DSM2 model output for the nine DSM2 output locations for which fish data were available. DSM2 data were not available at or near Vietnam Veterans Memorial Bridge on the Sacramento River or Vernalis on the San Joaquin River. Historical data of selenium concentrations in water collected near these locations were used to represent quarterly averages. The geometric mean of total selenium concentrations in water collected from years 2003, 2004, 2007, and 2008 (California Department of Water Resources 2009) at Knights Landing were used to represent quarterly averages of selenium concentrations in water for all years. The geometric means of selenium concentrations (*total* or *dissolved* was not specified) in water collected from years 1999–2007 (Central Valley Regional Water Quality Control Board 2009) were used to represent quarterly averages for all years of selenium concentrations in water at Vernalis.

The quarterly waterborne selenium concentrations at DSM2 locations were calculated using the following equation:

$$C_{water quarterly} = \frac{(I_1 \cdot C_1) + (I_2 \cdot C_2) + (I_3 \cdot C_3) + (I_4 \cdot C_4) + (I_5 \cdot C_5) + (I_6 \cdot C_6)}{100}$$
[Eq.1]

Where:

 $C_{water quarterly}$  = quarterly average selenium concentration in water (µg/L) at a DSM2 output location

 $I_{1-6}$  = modeled quarterly inflow from each of the six sources of water to the Delta for each DSM2 output location (percentage)

 $C_{1-6}$  = selenium concentration in water (µg/L) from each of the six inflow sources to the Delta (1-6)

Example Calculation: Modeled Selenium Concentration at Franks Tract Year 2000, First Quarter:

(43.94 [% inflow from Sacramento River water source at Franks Tract] × 0.32 μg/L [Selenium concentration at Sacramento River at Freeport]) + (11.56 [% inflow from East Delta Tributaries water source at Franks Tract]× 0.10 μg/L [Selenium concentration at Mokelumne, Calaveras, and Cosumnes Rivers]) + (15.79 [% inflow from San Joaquin River water source at Franks Tract] × 0.84 μg/L [Selenium concentration at San Joaquin River at Vernalis]) + (0.02 [% inflow from Martinez/Suisun Bay water source at Franks Tract] × 0.09 μg/L [Selenium concentration at San Joaquin River near Mildred Island]) + (0.32 [% inflow from Yolo Bypass water source at Franks Tract] × 0.45 μg/L [Selenium concentration at Sacramento River at Knights Landing]) + (5.06 [% inflow from Delta Agriculture water source at Franks Tract] × 0.11 μg/L [Selenium concentration at Mildred Island, Center])/100 = 0.29 μg/L

The quarterly and average annual waterborne selenium concentrations for the DSM2 output locations were calculated for Year 2000, Year 2005, and Year 2007.

# 4.B.3 Bioaccumulation of Selenium into Whole-Body Fish and Bird Eggs

Selenium concentrations in whole-body fish and bird eggs were calculated using ecosystem-scale models developed by Presser and Luoma (2010). The models were developed using biogeochemical and physiological factors from laboratory and field studies; information on loading, speciation, and transformation to particulate material; bioavailability; bioaccumulation in invertebrates; and trophic transfer to predators. Important components of the methods included (1) empirically determined environmental partitioning factors between water and particulate material that quantify the effects of dissolved speciation and phase transformation; (2) concentrations of selenium in living and nonliving particulates at the base of the foodweb that determine selenium bioavailability to invertebrates; and (3) selenium biodynamic foodweb transfer factors that quantify the physiological potential for bioaccumulation from particulate matter to consumer organisms and prey to their predators.

#### 4.B.3.1 Selenium Concentration in Particulates

Phase transformation reactions from dissolved to particulate selenium are the primary form by which selenium enters the foodweb. Presser and Luoma (2010) used field observations to quantify the relationship between particulate material and dissolved selenium as shown below.

 $C_{particulate} = K_d \cdot C_{water\ column}$ 

[Eq. 2]

Where:

 $C_{particulate}$  = selenium concentration in particulate material (micrograms/kilogram, dry weight [ $\mu$ g/kg dw])

 $C_{water column}$  = selenium concentration in water column (µg/L)

 $K_d$  = particulate/water ratio

The  $K_d$  describes the particulate/water ratio at the moment the sample was taken and should not be interpreted as an equilibrium constant (as it sometimes is). It can vary widely among hydrologic environments and potentially among seasons (Presser and Luoma 2010). In addition, other factors such as speciation, residence time, and particle type affect  $K_d$ . Residence time of selenium is usually the most influential factor on the conditions in the receiving water environment. Short water-residence times (e.g., streams, rivers) limit partitioning of selenium into particulate material. Conversely, longer residence times (e.g., sloughs, lakes, estuaries) allow greater uptake by plants, algae, and microorganisms. Furthermore, environments in downstream portions of a watershed can receive cumulative contributions of upstream recycling in a hydrologic system. Because of its high variability,  $K_d$  is a large source of uncertainty in the model, especially if translation of selenium concentration in the water column is necessary.

#### 4.B.3.2 Selenium Concentrations in Invertebrates

Species-specific trophic transfer factors (TTFs) for transfer of selenium from particulates to prey and to predators were developed using data from laboratory experiments and field studies (Presser and Luoma 2010). TTFs are species-specific, but the range of TTFs for freshwater invertebrates was found to be similar to TTFs for marine invertebrates determined in laboratory experiments.

TTFs for estimating selenium concentrations in invertebrates were calculated using the following equation:

$$TTF_{invertebrate} = \frac{C_{invertebrate}}{C_{particulate}}$$

[Eq. 3]

4 Where:

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- 5  $TTF_{invertebrate}$  = trophic transfer factor from particulate material to invertebrate
- 6  $C_{invertebrate}$  = concentration of selenium in invertebrate (µg/g dry weight [dw])
- 7  $C_{particulate}$  = concentration of selenium in particulate material (µg/g dw)
- 8 A mean aquatic insect TTF was calculated from TTFs for aquatic insect species with similar
- 9 bioaccumulative potential, including mayfly (Baetidae, Heptageniidae, Ephemerellidae), caddisfly
- 10 (Rhyacophilidae Hydropsychidae), crane fly (Tipulidae), stonefly (Perlodidae/Perlidae,
- 11 Chloroperlidae), damselfly (Coenagrionidae), corixid (*Cenocorixa* spp.), and chironomid
- 12 (*Chironomus* spp.) aquatic life stages. Species-specific TTFs ranged from 2.14 to 3.2 with a mean TTF
- 13 of 2.8.

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# 4.B.3.3 Selenium Concentrations in Whole-Body Fish

- The mechanistic equation for modeling selenium bioaccumulation in fish tissue is similar to that of
- invertebrates if whole-body concentrations are the endpoint (Presser and Luoma 2010), as follows:

$$TTF_{fish} = \frac{C_{fish}}{C_{invertebrate}}$$

Where:

[Eq. 4]

Therefore:

$$C_{fish} = C_{particulate} \cdot TTF_{invertebrate} \cdot TTF_{fish}$$

- Where:
- $C_{fish}$  = concentration of selenium in fish ( $\mu$ g/g dw)
- 20  $C_{invertebrate}$  = concentration of selenium in invertebrate ( $\mu g/g \, dw$ )
- 21  $C_{particulate}$  = concentration of selenium in particulate material (µg/g dw)
- 22 TTF<sub>invertebrate</sub> = trophic transfer factor from particulate material to invertebrate
- 23  $TTF_{fish}$  = trophic transfer factor from invertebrate to fish
- Modeling of bioaccumulation into a particular fish species includes physiology of the organism and its preferred foods. Therefore, variability in fish tissue concentrations of selenium is driven more by

1	dietary choices and their respective levels of bioaccumulation (i.e., TTF <sub>invertebrate</sub> ) than by differences
2	in the dietary transfer to the fish $(TTF_{fish})$ . A diet of mixed prey (including invertebrates or other
3	fish) can be modeled as follows:

 $C_{fish} = TTF_{fish} \bullet \left[ \left( C_1 \bullet F_1 \right) + \left( C_2 \bullet F_2 \right) + \left( C_3 \bullet F_3 \right) \right]$ [Eq. 5]

5 Where:

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- 6  $C_{fish}$  = concentration of selenium in fish ( $\mu$ g/g dw)
- 7  $TTF_{fish}$  = trophic transfer factor for fish species
- 8  $C_{1-3}$  = concentration of selenium in invertebrate or fish prey items 1, 2, and 3 (µg/g dw)
- 9  $F_{1-3}$  = fraction of diet composed of prey items 1, 2, and 3

Modeling of selenium concentrations in longer foodwebs with higher trophic levels (e.g., forage fish being consumed by predator fish) can be completed by incorporating additional TTFs; for example:

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$$C_{predator\ fish} = TTF_{invertebrate} \cdot C_{particulate} \cdot TTF_{forage\ fish} \cdot TTF_{predator\ fish}$$
 [Eq. 6]

- Where:
- 14  $C_{predator fish}$  = concentration of selenium in fish (µg/g dw)
- $TTF_{invertebrate}$  = trophic transfer factor from particulate material to invertebrate
- 16  $C_{particulate}$  = concentration of selenium in particulate material (µg/g dw)
- $TTF_{forage\ fish}$  = trophic transfer factor for invertebrates to foraging fish species
- 18  $TTF_{predator fish}$  = trophic transfer factor for forage fish to predator species
- The fish TTFs reported in Presser and Luoma (2010) ranged from 0.5 to 1.6, so the average fish TTF of 1.1 was used for all trophic levels of fish.
- 21 Modeled selenium concentrations in whole-body fish were used to estimate selenium
- concentrations in fish fillets, as described below.

# 4.B.3.4 Selenium Concentrations in Bird Eggs

Selenium concentrations in bird tissues can be estimated, but the transfer of selenium into bird eggs is more meaningful for evaluating reproductive endpoints (Presser and Luoma 2010). Examples of models for selenium transfer to bird eggs are as follows:

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- Where:
- 31  $C_{bird\ egg}$  = concentration of selenium in bird egg ( $\mu$ g/g dw)
- 32  $C_{particulate} = \text{concentration of selenium in particulate material } (\mu g/g dw)$
- 33 TTF<sub>invertebrate</sub> = trophic transfer factor from particulate material to invertebrate

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1  $TTF_{fish}$  = trophic transfer factor from invertebrate to fish

2  $TTF_{bird\,egg}$  = trophic transfer factor from invertebrate or fish (depending on diet) to bird egg

The only bird TTF presented in Presser and Luoma (2010) was for the mallard ( $TTF_{bird\ egg} = 1.8$ ).

Mallards are considered a species sensitive to selenium based on reproductive endpoints.

# 4.B.4 Refinement of Selenium Bioaccumulation Models for the Delta

Several models were evaluated and refined to estimate selenium uptake in fish and in bird eggs from waters in the Delta. Input parameters to the model ( $K_d$ s and TTFs) were varied among the models as refinements were made. Rationale for each refinement is presented below with the discussion of each model. In addition, largemouth bass collected in the Delta from areas near DSM2 output locations were used to calculate the geometric mean selenium concentration in whole-body fish (Foe 2010a). The ratio of the estimated selenium concentration in fish to measured selenium in whole-body bass was used to evaluate each fish model and to focus refinements to the model. The models evaluated are presented in the following subsections.

## 4.B.4.1 Bioaccumulation in Whole-Body Fish

- Seven models were evaluated for estimating whole-body selenium concentrations in fish. The basic models were refined by dietary fraction and input parameters to provide a model that would most closely represent conditions in the Delta. Each model is described in this section.
- Model 1 was a basic representative of uptake by a forage fish, and Models 2 and 3 calculated sequential bioaccumulation in longer foodwebs representative of predatory fish of increasing complexity as shown below:
- 22 Model 1: Trophic level 3 (TL-3) fish eating invertebrates

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$$C_{fish} = C_{particulate} \cdot TTF_{invertebrate} \cdot TTF_{fish}$$
 [Eq. 9]

$$C_{fish} = C_{particulate} \bullet TTF_{invertebrate} \bullet TTF_{fish} \bullet TTF_{fish}$$
[Eq. 10]

26 Model 3: TL-4 fish eating TL-3 fish eating TL-3 and TL-2 invertebrates

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$$C_{fish} = C_{particulate} \cdot TTF_{invertebrate} \cdot TTF_{invertebrate} \cdot TTF_{fish} \cdot TTF_{fish}$$
 [Eq. 11]

Where:

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- $C_{fish}$  = concentration of selenium in fish (µg/g dw)
- 30  $C_{particulate}$  = concentration of selenium in particulate material ( $\mu g/g \, dw$ )
- 31  $TTF_{invertebrate}$  = Trophic transfer factor from particulate material to invertebrate
- 32  $TTF_{fish}$  = Trophic transfer factor from invertebrate or fish to fish
- In each model, the particulate selenium concentration was estimated using Equation 2 and a default  $K_d$  of 1,000. The average TTFs for invertebrates (2.8) and fish (1.1) were used in each model. The

- 1 outputs of estimated selenium concentrations and the ratios of estimated fish selenium
- 2 concentration to measured bass selenium concentration for Models 1, 2, and 3 were calculated.
- 3 Model 1 tended to underestimate the whole-body selenium concentrations in fish compared to bass
- 4 data reported in Foe (2010a). This was most likely because Model 1 was estimating a forage fish
- 5 (TL-3), whereas bass are a predatory fish with expected higher dietary exposure. Consequently,
- 6 Model 1 was not developed further as the selenium bioaccumulation model to represent fish in the
- 7 Delta.

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- 8 Models 2 and 3 are both representative of predatory fish, but Model 2 was very similar to Model 1 in
- 9 distribution of data and in underestimating bass data. Conversely, Model 3 had a larger distribution
- 10 and greater variation in the data and significantly overestimated the bass data. These models were
- 11 used as the basis for Models 4 and 5.
- 12 Models 4 and 5 were developed to represent a mixed diet using prey fractions to characterize the
- 13 diet of fish in the Delta, as follows:
- 14 Model 4: 50% of Model 2 and 50% of Model 3

$$C_{fishModel 4} = (0.5 \cdot C_{fishModel 2}) + (0.5 \cdot C_{fishModel 3})$$
[Eq. 12]

Model 5: 75% of Model 2 and 25% of Model 3 16

Model 5: 75% of Model 2 and 25% of Model 3
$$C_{fishModel5} = (0.75 \cdot C_{fishModel2}) + (0.25 \cdot C_{fishModel3})$$
[Eq. 13]

- Models 4 and 5 used the default  $K_d$  (1,000), average invertebrate TTF (2.8), and average fish TTF (1.1). The outputs of estimated selenium concentrations and ratios of the estimated selenium concentration in fish to measured selenium concentration in bass data for Models 4 and 5 were calculated. Data distribution and variation were comparatively large in Model 4. Model 5 was relatively predictive of bass data but was not considered representative of the general population of predatory fish in the Delta. Consequently, it was determined that Model 2 was the most representative of the prey base used by fish in the Delta (i.e., number of trophic levels in the model); therefore, further evaluation and refinement of the selenium bioaccumulation model was limited to Model 2.
- In addition, review of Models 1 through 5 indicated that the default value of 1,000 for  $K_d$  was not representative of the Delta's potentially high variability and uncertainty with regard to residence time. The Delta tends to have a long water-residence time and receives upstream contributions of selenium, and greater recycling and higher concentrations of selenium entering the foodweb are expected. Model 6 was developed using an extrapolated  $K_d$  value of 1,400 with Model 2 (Equation 10). The average invertebrate and fish TTFs were used. Model 6 was generally predictive of bass data (ratio median 1.04). The outputs of estimated selenium concentrations and ratios of the estimated selenium concentration in fish to measured selenium concentration in bass data for Model 6 were calculated.
- 36 Model 7 was a further refinement whereby site-specific data for dissolved selenium in water and 37 selenium in particulate samples collected in the Delta (Lucas and Stewart 2007) were used to 38 calculate a site-specific  $K_d$  of 1,760 (geometric mean). Model 7 used the more representative site-39 specific  $K_d$  (1,760) with Model 2 (Equation 10) and the average invertebrate and fish TTFs (2.8 and 40 1.1, respectively). The outputs from Model 7 slightly overestimated selenium concentrations in fish 41 compared to selenium concentrations in bass (ratio median 1.30).

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Model 8 used the site-specific  $K_d$  (1,760) and the average fish TTF (1.1). The invertebrate TTF was revised so that mayflies and stoneflies were not included in the average, because these species would not be readily available in the Delta to contribute to fish or bird diets. The revised invertebrate TTF of 2.1 was used in Model 8.

As expected in a large, complex, and diverse ecological habitat such as the Delta, variations in the data distribution and in the outputs of all models including Model 8 (minimum ratio 0.45, maximum ratio 2.21, and median ratio 0.98) were observed. The variation in the models' outputs is influenced primarily by (1) the selenium concentration in water, used to estimate the selenium concentration in fish tissue, and (2) the measured selenium concentration in bass. Variation in selenium concentrations in water among the years was small, so the variation in selenium concentrations in bass was the primary factor determining the temporal variation among the models. One prominent outlier was observed in all models, seasons, and years as shown by the overestimation of selenium concentration in fish to measured selenium in bass collected at Vernalis. The overestimation is likely the result of high selenium concentrations in water calculated during different years (1999–2007) from those when bass were collected (2000, 2005, and 2007).

Data from Year 2000 were the most predictive in estimating selenium concentrations in fish tissue compared to measured selenium concentrations in bass with Model 8 (minimum ratio = 0.53, maximum ratio = 2.21, and median ratio = 0.98). Foe (2010a) reported the water-year type for 2000 as "above normal" for both the Sacramento River and San Joaquin River watersheds. It came after wet water years and was followed by dry water years. Year 2005 selenium concentrations in bass were comparatively lower than those estimated for Year 2000. Year 2005 was wetter than Year 2000 (reported as above normal for the Sacramento River watershed and wet for the San Joaquin River watershed) and occurred between periods of wetter water years than reported for Year 2000. As expected in a wet water year, the water-residence time is shorter, resulting in less selenium recycling and lower concentrations of selenium entering the foodweb. Under these influences, Model 8 tended to overestimate selenium concentrations in fish for Year 2005 (minimum ratio = 0.79, maximum ratio = 2.12, and median ratio = 1.21). For Year 2007, the model generally underestimated the comparatively higher measured selenium concentration in bass (minimum ratio = 0.45, maximum ratio = 1.57, and median ratio = 0.62). Water Year 2007 was reported as dry (Sacramento River watershed) and critically dry (San Joaquin River watershed). It came after wet water years and was followed by critically dry water years. This dry water year resulted in a longer waterresidence time, greater selenium recycling, and higher concentrations of selenium entering the foodweb. Because the influences of a dry water year were not captured in the selenium concentrations in water and were reflected only in bass, Model 8 underestimated selenium concentrations in bass for Year 2007. Therefore, these results illustrate how Model 8 best predicts selenium concentration in fish during normal to wet water years but not dry water years. However, as shown above, Model 8 also can represent selenium bioaccumulation when all water-year types are combined (represented by 2000, 2005, and 2007).

Further evaluation of water-year effects on selenium concentration in bass concluded that a more representative model was needed for dry water years. Therefore, Model 9 used an extrapolated  $K_d$  of 2,840, the revised invertebrate TTF of 2.1, and the average fish TTF of 1.1 with Model 2 to provide a better fit for the bass data in dry water years. The outputs of estimated selenium concentrations and ratios of the estimated selenium concentration in fish to measured selenium concentration in bass data for Model 9 were calculated.

January 2012

ICE 00610 10

- 1 Model 8 is relatively predictive of selenium concentration in whole-body bass during normal to wet
- 2 water years (ratio median 1.04) for all water years (ratio median 0.98) and Model 9 is considered
- 3 predictive for dry water years (ratio median 1.00) These models were selected as the selenium
- 4 bioaccumulative models to estimate selenium concentration in whole-body fish in the Delta and are
- 5 summarized below for ease of reference.
- 6 Model 8: Trophic level 4 (TL-4) fish eating TL-3 fish

$$C_{fish} = C_{particulate} \bullet TTF_{invertebrate} \bullet TTF_{fish} \bullet TTF_{fish}$$

 $C_{particulate} = K_d \cdot C_{water}$ 

$$C_{fish} = C_{particulate} \bullet TTF_{invertebrate} \bullet TTF_{fish} \bullet TTF_{fish}$$

9 Where: [Eq. 15]

$$C_{particulate} = K_d \cdot C_{water}$$

- Where:
- 11  $C_{particulate}$  = Concentration of selenium in particulate material (µg/g dw)
- 12  $C_{water}$  = selenium concentration in water column (µg/L)
- $K_d = \text{equilibrium constant}$
- $TTF_{invertebrate}$  = Trophic transfer factor from particulate material to invertebrate
- $TTF_{fish}$  = Trophic transfer factor from invertebrate to fish
- 16 Because all models greatly overestimated selenium bioaccumulation in fish at Vernalis in all seasons
- and years, Models 8 and 9 were modified by adjusting the  $K_d$  downward to reflect the lower rate of
- bioaccumulation at that location. The adjusted models used  $K_d$  values of 850 for Model 8a and 1,130
- for Model 9a. With these adjustments, Model 8a produced a ratio of 1.01 for the comparison of
- modeled fish to the bass data, and Model 9a produced a ratio of 1.00.

# 21 4.B.4.2 Bioaccumulation in Bird Eggs

- The  $K_d$ , invertebrate TTF, and fish TTFs developed for use in fish bioaccumulation Models 8 and 9
- also were used to estimate selenium uptake into bird eggs using the following two bird egg models:
- 24 Bird Egg: Uptake from invertebrates

 $C_{particulate} = K_d \cdot C_{water}$ 

26 Bird Egg: Uptake from fish

 $C_{particulate} = K_d \cdot C_{water}$ 

1	Where:
2	$C_{bird\ egg}$ = concentration of selenium in bird egg (µg/g dw)
3	$C_{particulate}$ = concentration of selenium in particulate material (µg/g dw)
4	$C_{water}$ = selenium concentration in water column ( $\mu$ g/L)
5	$K_d$ = equilibrium constant
6	$TTF_{invertebrate}$ = trophic transfer factor from particulate material to invertebrate
7	$TTF_{fish}$ = trophic transfer factor from invertebrate to fish
8	$TTF_{birdegg}$ = trophic transfer factor from invertebrate or fish (depending on diet) to bird egg
9 10	For normal to wet years, the site-specific $K_d$ value (1,760), revised invertebrate TTF (2.1), average fish TTF (1.1), and mallard bird egg TTF (1.8) were used. For dry years, the revised $K_d$ (2,840),

## 4.B.5 Bioaccumulation in Fish Fillets

Selenium concentrations in whole-body fish were converted to selenium concentrations in skinless fish fillets. The regression equation provided by Saiki and coauthors (1991) for largemouth bass from the San Joaquin River system was considered to be the most representative of fish in the Delta and was used for the conversion of these selenium concentrations as follows:

revised invertebrate TTF (2.1), average fish TTF (1.1), and mallard bird egg TTF (1.8) were used..

$$SF = -0.388 + 1.322 WB$$
 [Eq. 18]

Where:

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SF = selenium concentration in skinless fish fillet (µg/g dw)

WB = selenium concentration in whole-body fish (µg/g dw)

Fish fillet data will be compared to the advisory tissue level (2.5  $\mu$ g/g) in wet weight (Office of Environmental Health Hazard Assessment 2008); therefore, wet-weight concentrations were estimated from dry-weight concentrations using the equation provided by Saiki and coauthors (1991) as follows:

$$WW = DW \cdot (100 - Moist)/100$$
 [Eq. 19]

Where:

WW = selenium concentration in wet weight (µg/g ww)

DW = selenium concentration in dry weight (µg/g dw)

*Moist* = mean moisture content of the species

Because moisture content in fish varies among species, sample handling, and locations, the mean moisture content of 70% as used by Foe (2010b) was used as an assumed approximation for fish in the Delta. The final equation used to estimate selenium concentration in skinless fish fillets (wet weight) from selenium concentration in whole-body fish (dry weight) is as follows:

$$SF = (-0.388 + 1.322 WB) \cdot 0.3$$
 [Eq. 20]

1	Where:

- 2 SF = selenium concentrations in skinless fish fillet ( $\mu$ g/g ww)
- 3  $WB = \text{selenium concentration in whole-body fish } (\mu g/g \text{ dw})$

### 4 4.B.6 References

#### 4.B.6.1 Printed References

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#### 4.B.6.2 Personal Communications

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- Valley Region, Rancho Cordova, CA. April 23, 2010—e-mail to Harry Ohlendorf, Technology
- Fellow, CH2M HILL, Sacramento, CA.